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Continuous supercritical synthesis of unsupported and high specific surface area catalyst precursors for deep-hydrodesulfurization

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ABSTRACT

Unsupported and high specific surface area (S_{BET}) catalyst precursors for deep-hydrodesulfurization (deep-HDS) are obtained using an environmental friendly, continuous and fast synthesis process in supercritical water/alcohol mixtures. This approach offers an access to high production rate and upscaling. Two mixed oxides were synthesized: $NiMoO_4$, which is the preferred material when deep-HDS is investigated, and $CoMoO_4$ preferred for simple HDS. The role of the water/alcohol mixture on the resulting specific surface area has been studied and allows a controlled adjustment of the resulting specific surface area. The obtained $NiMoO_4$ material consists of the highly active hydrate $NiMoO_4.0.75H_2O$ phase with a controlled composition and specific surface area up to 200 $m^2\,g^{-1}$. Resulting materials have shown great performances when tested in deep-HDS catalytic tests.

1. Introduction

Due to increasingly stringent environmental regulations in sulfur limits for distillates fuels, production of ultra-low sulfur content fuels is required to reach the limits of 10 ppm in the European Union [1] and Japan [2] and 15 ppm in North America [3]. Moreover, remaining available crude oil resources contain a greater amount of undesirable heteroatoms that will have to be removed. Removal of 99.99% of sulfur from typical crude oil and the corresponding processes have been termed as deep-HDS. The main issue of deep-HDS is the elimination of refractory sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT). In order to achieve this issue without expensive costs in process modifications, the development of more efficient deep-HDS catalysts is required.

Typically, a HDS catalyst contains a metal from the group VIB (chromium, molybdenum or tungsten) promoted with a metal from the group VII (cobalt or nickel) and supported, classically, on alumina [4–6]. These conventional catalysts are generally obtained by impregnation of γ-Al_2O_3 with aqueous solutions of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$ followed by drying, calcination and activation under H_2/H_2S [7] in order to obtain MoS_2 layers well dispersed on the γ-Al_2O_3 support and edges-decorated with Co or Ni [8]. However, current HDS catalysts revealed to be insufficient and strong optimizations have been investigated over the past decades, such as improvement of the support and/or of the active phase [9].

On the other hand, some unsupported materials have been described with higher activity and/or selectivity than traditional supported catalysts, leading to a growing interest in unsupported HDS nano-catalysts [10–19]. This category of catalysts can easily be obtained by thermal decomposition [20,21], metal amines metallates [15], hydrothermal [22], citrate [23], freeze-drying [24] and impregnation [25] for the most classical methods. However, their main weakness compared to supported catalysts is their low specific surface area (S_{BET}), down to 10–80 $m^2\,g^{-1}$ for most of the unsupported catalysts [15,20,25–28]. However recent works have reported maximum values for S_{BET} around 200–300 $m^2\,g^{-1}$ [29,30], similar than those presented by alumina supported catalysts (200–300 $m^2\,g^{-1}$) [31].

Increasing S_{BET} appears to be a very interesting challenge in the development of this new generation of catalysts but most of the time, high S_{BET} unsupported catalyst synthesis generates toxic compounds and therefore is difficult to implement at industrial scale [30]. In order to do so, supercritical fluids technologies are known to be efficient to prepare highly dispersed nanostructures [32] and nanopowders with high S_{BET} [33,34] without generation

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of toxic compounds. In this work we propose the use of green solvents (water/alcohols), inexpensive (ten times cheaper than the ones use in conventional methods for high S_{BET} materials [30]) and friendly precursors. Moreover, our approach allows the synthesis of crystalline materials with controlled and adjustable compositions [35–38] but also with a tuneable specific surface area [33] by playing with the carbon length of the alcohol used. These materials are produced in a fast, sustainable and continuous process which is a major asset for upscaling [39]. All these advantages are obviously linked to the good activities of our materials in deep-HDS. Our catalyst precursors have shown a similar activity in removing the most refractory compound (4,6-DMDBT) to those of a reference catalyst but at reaction temperature 40 °C lower. As far as we know, the use of this method to synthesize $Ni(Co)MoO_4$ has not been so far reported in the literature.

2. Materials and methods

2.1. Materials precursors

Bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(CH_3COCHCOCH_3)_2$, Alfa Aesar, 99%), nickel(II) acetate tetrahydrate ($Ni(CH_3COO)_2{\cdot}4H_2O$, Alfa Aesar, 99%) and cobalt(II) acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$, Alfa Aesar, 98%) were used without further purification.

2.2. Synthesis procedures

The starting Ni(Co)- and Mo-containing solutions were prepared as follow: Mo salt was dissolved in a water/alcohol mixture of molar ratio 1:1 and Ni(Co) precursor was previously dissolved in distilled water before adding the same quantity of alcohol in order to prevent the precipitation due to alcohol aversion of the acetate. The alcohols used in this study were methanol, ethanol and isopropanol. Molybdenum concentration was fixed at $[Mo] = 7.2.10^{-3}$ mol L^{-1} and Ni concentration was adjusted to vary the metal molar ratios (36–50–57–60–66 at%). For cobalt, the concentration used was equal to the one of Mo. The solutions of precursors are pumped using high pressure pumps and are mixed before the entrance of the reactor. The tubular reactor (8 m of length and an inner diameter of 1.32 mm) is heated using a heater band and the pressure is controlled using a back pressure regulator (BPR). Before the back pressure regulator, an ice bath permits to quench the reaction and to recover the particles into a filter. The experimental set-up is presented in Fig. 1.

Reactions have been carried out at a temperature of 290 °C and a pressure of 23 MPa. To verify if the mixtures alcohols/water were in supercritical conditions at these temperature and pressure, the critical coordinates of these mixtures have been estimated using a microfluidic approach [41]. Supercritical coordinates of these mixtures can be found in Table S1 in S.I. In order to keep a constant residence time for all experiments (55s) [36,37], the flow rate was calculated using the following relation:

$$\tau = \frac{V_{reactor}}{Q_{tot}} * \frac{\rho_{conditions}}{\rho_{pump}}$$

with τ: the residence time in s, $V_{reactor}$: the volume of the reactor (8.2 mL), Q_{tot}: the total flow rate in mL s^{-1}, $\rho_{conditions}$: the density of the mixture at 290 °C and 23 MPa and ρ_{pump}: the density of the mixture at room temperature and 23 MPa.

A chemical reaction takes place leading to the nucleation and growth of the NiMo or CoMo nanoparticles. These last ones followed their way to a filter deepened in an ice bath to quench their growth. The obtained powder was washed with distilled water, recovered by vacuum filtration and dried at room temperature before a thermal treatment at 400 °C for 3 h.

2.3. Characterization techniques

Metal ratios were determined by Inductively Coupled Plasma/Optical Emission Spectrometry (ICP-OES) using a Varian 720-ES equipment. Carbon pollutions were detected using CHNS-O analysis, accomplished by combustion analysis according to the Pregl-Dumas procedure. The equipment used was a Flash EH 1112 from Thermo Fisher.

X-Ray powder diffraction (XRD) patterns were obtained from a Philips PW1820 and a PANalytical XíPert X-Ray diffractometers in Bragg-Brentano geometry equipped with Cu Kα1 source and an XíCelerator detector. Diffraction patterns were collected with a 2θ step of 0.02° and a 0.0358° s^{-1} scan speed routine mode; for more advanced investigations a 0.008° step and a 0.0053°.s^{-1} scan speed were used on a PANalytical XíPert pro MOO equipped with primary Ge (111) monochromator Cu Kα1 source. The cell fitting, and thus the cell volume, were obtained by profile fitting of the pattern with the FULLPROF program. The fits were performed using a pseudo-Voigt peal-shape function. In the final runs, the usual profile parameters (scale factors, background coefficients, zero point, half-widths, pseudo-Voigt and asymmetry parameters for the peak shape) were refined.

The morphology of the powders was observed using a scanning electron microscope (JEOL 6700F) operating at an accelerating voltage of 30 kV. The size of the nanoparticles was evaluated using a high-resolution transmission electron microscope (JEOL JEM-2200FS) enable to switch to a scanning mode to make chemical X-Ray mapping of nanoparticles.

Physisorption measurements were performed using an Autosorb-1 instrument from Quantachrome. The BET specific areas were determined by N_2 adsorption at 77 K assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule. Prior to adsorption measurements, the samples were outgassed in a vacuum at room temperature for 2 h.

2.4. Catalytic tests

The model feedstock used was composed of 60 wt% of paraffins, 30 wt% of olefins and 10 wt% of aromatic hydrocarbons, in order to deal with a possible "matrix effect". The detailed composition can be found in Table S4 enclosed in S.I. The total sulfur content was 500 wppm with 100 wppm as 4,6-DMDBT, the most refractory compound. No nitrogen compounds were added to the feedstock in order to avoid the competition with HDN.

The activity tests were conducted in a fixed bed tubular reactor. The reactor was charged with 160 μL of catalyst (pelletized at a diameter comprised between 0.250 μm and 0.425 μm) and diluted in SiC (diluent/catalyst volume ratio of 12). The activation of the catalyst was done in situ using a mixture of H_2S/H_2 with 10 vol% H_2S at an atmospheric pressure and a temperature of 400 °C for 3 h. The reaction conditions were the following: total pressure of 3.5 MPa, temperature of reaction between 320 and 400 °C, Liquid Hourly Space Velocity (LHSV) of 39 h^{-1} and a ratio H_2/feed of 5. For each test, liquid samples were accumulated, weighted and analyzed at intervals of about 40 min. For all catalysts, a constant composition of the reactor outlet stream was observed after reaction periods of 3–4 h. Results reported in this work correspond to the steady-state period of operation. The composition of feed and products was analyzed by gas chromatography in a Varian 3800 equipped with a 30 m column (VF 5 ms CP8944) with an inner diameter of 0.25 mm and a bonded stationary phase made of a 0.25 μm thick film of (5% phenyl, 95% dimethyl) polysiloxane, and two detectors, a Flame Ionization Detector and a sulfur specific Pulsed Flame Photometric Detector.

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