Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 130 (2008) 56–62

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Highly dispersed CoMoS phase on titania nanotubes as efficient HDS catalysts

M.A. Cortés-Jácome, J. Escobar, C. Angeles Chávez, E. López-Salinas, E. Romero, G. Ferrat, J.A. Toledo-Antonio *

Molecular Engineering Program, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas #152,
San Bartolo Atepehuacan, G.A. Madero, 07730 México, D.F., Mexico

Abstract

Nanotubular titania (NT) to be used as support for CoMo-based hydrodesulfurization (HDS) catalyst was synthesized and characterized by various techniques. NT annealed at 400 °C (under nitrogen) was constituted by nanotubes of ~5.5 nm (internal diameter) and retained 236 m^2/g of surface area. Mo at 3 atoms/nm^2 (nominal loading) and cobalt at Co/(Co + Mo) = 0.3 were impregnated under nearly neutral, acidic or basic media. By XPS analyses of NT-supported sulfided catalysts, highly dispersed MoS_2 particles of low stacking degree (1–2 slabs) aligned along the nanotubes were observed by HR-TEM in all sulfided materials. The CoMo catalysts supported on nanostructured titania had dibenzothiophene (DBT) HDS activity (in pseudo first order kinetic constant basis) values ~1.35 and ~1.7 times (Mo impregnated under near neutral and basic media, respectively) higher to that of a commercial reference with alumina carrier. According to shifts to higher binding energy of the Co 2p peak corresponding to sulfided cobalt (as determined by XPS), MoS_2 dispersed on NT support could be efficiently promoted by Co (“CoMoS” phase formation), opening the possibility of developing new highly active HDS catalysts.

Keywords: HDS catalysts; Titania; CoMoS; XPS; HRTEM; Nanotubes support

1. Introduction

The more stringent environmental regulations that limit maximum sulfur content in diesel at ~10–15 wt ppm, have been the driving force for refiners to produce ultra-low sulfur fuels at affordable costs either by upgrading existing technologies or by developing new oil refining processes, including more active hydrodesulfurization (HDS) catalysts. The application of more active catalytic materials could result in improvements in fuel quality without negative impact on capital investment.

Industrially, HDS of middle distillates is carried out on sulfided either CoMo/Al_2O_3 or NiMo/Al_2O_3 catalysts. The properties of those sulfided catalysts strongly depend on the interaction of the impregnated phases with the support that in turn, could influence dispersion, sulfidability and promotion degree of MoS_2 by neighboring Co and Ni. These facts could determine the efficiency of the formation of the so called “CoMoS” or “NiMoS phase” [1,2], in which S vacancies occurring at edge/corner sites of MoS_2 crystallites are considered to be the active sites for HDS reactions. When supported on alumina, these sites were formerly classified as “Type I” when located in sulfided Mo exhibiting lower S coordination and high dispersion of MoS_2 slabs [3]. On the other hand, when this phase was less dispersed and fully sulfided “Type II” sites were present [3]. CoMoS Type II sites are reported to be more active than Type I ones [3]. Highly active CoMoS Type II sites of low stacking degree can be obtained by replacing the alumina support by other carriers, such as carbon, showing weaker interaction with the impregnated phases [3]. One of the most promising supports for HDS catalysts is titania, due to the enhanced activity that have been observed for the corresponding sulfided catalysts [4,5]. Accordingly, TiO_2 with relative high surface area (e.g. 120–160 m^2/g) has been developed with improved textural properties, the carrier being able to efficiently disperse Mo [5] or Co–Mo phases [6]. The corresponding CoMo/TiO_2 formulation enabled the production of ultra low sulfur diesel

---

* Corresponding author. Tel.: +52 55 91 75 8433.
E-mail address: jtoledo@imp.mx (J.A. Toledo-Antonio).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.07.012

(ULSD) of ~10 ppm S at operating conditions at which over an alumina supported commercial reference a S content of about 200 ppm was observed in the diesel product. Recently, we synthesized high surface area (>300 m^2/g) nanotubular titania (NT) where the supported CoMoS phase was both highly dispersed and highly sulfided, these characteristics being reflected in enhanced activity in DBT HDS [7]. In the present contribution, the effect of the pH of the impregnating solution on the CoMoS phase dispersion was studied in materials at 3 Mo at./nm^2 nominal loading on the NT support.

2. Experimental

2.1. Synthesis of support

NT support was synthesized by a hydrothermal method as described in [8], starting from a TiO_2 anatase (Hombitec K03, provided by Sachtleben Chemie). TiO_2 anatase powder was suspended in an aqueous 10 M NaOH solution and the resulting suspension was placed in an autoclave at 100 °C for 24 h under stirring. Thereafter, the white slurry was filtered and neutralized with 1 M HNO_3 overnight. Then, the material was washed and dried at 110 °C yielding a hydrous titania powder with nanotubular morphology.

2.2. Catalysts preparation

CoMo-based catalysts were prepared from high surface area NT by impregnation at incipient wetness. For all materials, the nominal Mo loading was 3 atoms/nm^2 taking into account the surface area of the dried support (369 m^2/g) meanwhile cobalt was added at Co/(Co + Mo = 0.3). In the first case, the carrier was contacted with aqueous ammonium heptamolybdate (AHM) solutions at natural pH (5.6, close to neutral, "N"). After drying at 120 °C, cobalt was deposited on the Mo-containing samples through a $(CH_3CO_2)_2Co\cdot 4H_2O$ solution. Another sample was prepared by Mo impregnation under basic ("B") conditions at pH 10.0, by addition of some drops of NH_4OH (28 vol.%) to the original AHM solution. In this case, Co was deposited following the procedure already mentioned for the previous formulation. Finally, a third sample was impregnated under acidic ("A") conditions in one step. The impregnating solution was prepared by digesting MoO_3 with cobalt acetate and phosphoric acid at 95 °C (all of them in aqueous solution). The final acidic solution had a pH ~1.8. For all impregnated materials, further processing included drying at 120 °C and annealing at 380 °C under air flow. Hereinafter the catalysts will be referred to as NTB-3, NTN-3 and NTA-3 where NT stands for the nanotubular support; B, N and A represents the conditions of Mo impregnation and the number 3 indicates the nominal amount of Mo atoms per nm^2. Catalysts sulfidation was carried out over oxidized samples under H_2S/H_2 10 vol.%. First, the solids were brought to 380 °C, under N_2 atmosphere (100 mL/min), and then the gas flow was switched to an in situ made H_2S/H_2 mixture (6/50 mL/min). These conditions were maintained during 1 h.

2.3. Catalysts evaluation

Sulfided catalysts (~0.2 g) were tested in HDS of model molecule (DBT, ~0.3 g) in a batch reactor using *n*-hexadecane as solvent (100 mL). The reaction conditions were 320 °C, 1000 rpm and 56 kg/cm^2 and sulfided catalysts were used as particles of 80–100 U.S. standard mesh size (~0.165 mm average particle diameter). These conditions were carefully chosen to avoid reaction control by internal/external diffusion phenomena. Liquid products were analyzed in a Varian 3400 CX gas chromatograph (FID detector and dimethylpolysiloxane capillary column, 50 m × 0.2 mm × 0.5 μm). HDS kinetic constants were calculated assuming pseudo-first order kinetics referred to DBT concentration (x = conversion, t = time):

$$k = \frac{-\ln(1-x)}{t}$$

2.4. Catalysts characterization

Textural properties of various materials were determined by N_2 physisorption (at −196 °C), in a Micromeritics ASAP 2000 apparatus. Chemical composition of the impregnated materials after annealing at 380 °C was determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer 2380 apparatus. Identities of crystalline phases in the annealed and sulfided materials were examined by X-ray diffraction. Patterns of the samples ($5 < 2\theta < 70°$) packed in a glass holder were recorded at room temperature with $Cu_{K\alpha}$ radiation (λ = 1.5406 Å) in a Siemens D-500 diffractometer with a graphite secondary beam monochromator. The $Cu_{K\alpha 1}$ contribution was eliminated by DIFFRAC/AT software. Raman spectra were recorded at room temperature using a Jobin Yvon Inc. Horiba T64000 spectrometer, equipped with a confocal microscope (Olympus, BX41) with a laser beam (514.5 nm) at a power level of 3 mW. Sulfided catalysts were also analyzed by X-ray photoelectronic spectroscopy (XPS). The corresponding spectra were obtained in a THERMO-VG SCALAB 250 spectrometer equipped with $Al_{K\alpha}$ X-ray source (1486.6 eV) and a hemispherical analyzer. Experimental peaks were decomposed into components using mixed Gaussian–Lorentzian functions and a non-linear squares fitting algorithm. Shirley background subtraction was applied. Binding energies were reproducible within ±0.2 eV and the C 1s peak (from adventitious carbon) at 284.6 eV was used as a reference. Surface elemental composition was determined by fitting and integrating the Co 2p, Mo 3d, S 2p, C 1s, O 1s and Ti 2p bands and converting these values to atomic ratios using theoretical sensitivity factors provided by the manufacturer of the XPS apparatus [9]. The sulfided catalysts were kept under inert atmosphere by using a glove box and a special box vessel to introduce the samples into the spectrometer analysis chamber. High-resolution transmission electron microscopy (HR-TEM) analysis of the samples was performed in a JEOL 2010F microscope operating at 200 kV, and equipped with a Schottky-type field emission gun and an ultrahigh resolution pole piece (Cs = 0.5 mm; point to point resolution, 0.190 nm). The support and sulfided catalysts were ground, suspended in