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Highly active CoMoS phase on titania nanotubes as new hydrodesulfurization catalysts

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ABSTRACT

A series of CoMoS on nanotubular TiO_2 (NT) catalysts were prepared by incipient impregnation at Mo = 3–5 atoms/nm^2 and Co/(Co + Mo) = 0.2–0.4. A nanotubular TiO_2 (NT) of 5.5 nm inner diameter, 236 m^2/g surface area and 0.5 cm^3/g total pore volume was prepared and used as support. The CoMoS/NT catalysts were characterized mainly by Raman and XPS spectroscopies, HRTEM and HAADF (high angle annular dark field) detector. The sulfided catalysts were tested in the hydrodesulphurization (HDS) of dibenzothiophene at 320 °C and 56 kg/cm^2. Inorganic fullerene-like MoS_2 and/or CoMoS particles, made up of 2–6 structural layers, depending on the Co/(Co + Mo) ratio, were observed, smeared along the nanotubes. An estimation of CoMoS phase surface density (δ), after taken into account all sulfided species quantified by XPS spectra, indicated that highest HDS activity (43×10^{-4} m^3/kg_{Mo} s) is attained when Mo = 5 atoms/nm^2 and Co/(Co + Mo) = 0.3. In comparison, at a lower (0.2) or higher (0.4) Co/(Co + Mo) ratio, either segregated MoO_3 or Co_9S_8 phases were detected, respectively, with Co sulfidability decreasing 60–42%, respectively, and HDS activity being considerably lower.

1. Introduction

The more stringent environmental regulations concerning maximum sulfur content in liquid fuels, e.g., <15 ppm, have been the driving force for oil refineries to produce ultra-low sulfur fuels at affordable cost, upgrading existing technologies and developing new processes and more active hydrodesulfurization (HDS) catalysts. The application of the later could enhance the productivity and improve the product quality without negative impact on capital investment.

Industrially, HDS reaction is carried out on CoMoS/Al_2O_3 or NiMoS/Al_2O_3 catalysts. The properties of the sulfided catalyst strongly depend on the interaction with the support and on the promotion degree of MoS_2 by the adjacent Co and Ni sulfides yielding the so called "CoMoS" or "NiMoS" phases, [1,2] which are considered to contain the active sites for HDS reactions. It has been reported that coordinatively unsaturated sites occur at edges and corners of MoS_2 crystallites. For alumina-supported catalysts the sites have been classified as type 1, when present on monolayer MoS_2 slabs, and type 2, when in highly stacked MoS_2 particles [3]. CoMoS type 2 sites are about twice as active as type 1 [4]. Then, the formation of highly dispersed CoMoS type 2 sites may result in highly active CoMo sulfided catalysts. However, CoMoS phase formation is not an easy task, and strongly depends on the interaction degree between Mo oxide (e.g., precursor to MoS_2) and the support. In alumina-supported catalysts for example, the surface is often modified with additives such as phosphorous, fluorine or boron [5,6] to adequately obtain improved Mo oxides dispersion, and in order to control morphology, size and stacking number of MoS_2 particles.

Other strategies applied to generate highly active CoMoS type 2 sites involve replacing the conventional alumina support by other metal oxides showing less interaction with deposited Mo oxides such as SiO_2 [7], TiO_2 [8,9], ZrO_2 [10] or mixed oxides [11,12]. Thus, great interest is being devoted to study the effect of the support on the HDS catalytic activity of CoMoS and NiMoS sulfided catalysts. One of the most interesting supports for HDS catalysts is titania, since a considerable increase in intrinsic HDS activity has been reported for MoS_2 when supported on anatase TiO_2, in comparison with a similar composition on an alumina carrier [8,13]. However, the TiO_2 low specific surface area (SSA) (e.g., <60 m^2/g) limits its industrial application as HDS catalyst support. Recently, TiO_2 with relatively high SSA (140–175 m^2/g) have been developed, with good enough textural properties to efficiently disperse CoMoS phase [14,15]. These improved formulations may have a beneficial impact on the production of ultra-low sulfur diesel (ULSD).

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In the last decade, anatase TiO_2 has been converted into titania nanotubes or nanofibers through a relatively simple alkaline hydrothermal method [16–19], representing a suitable route for rapid manufacturing scale-up. The nanotubes exhibit large internal and external surfaces, along with surface in the vertex and in the interlayer regions that compose the nanotube walls [20,21]. In fact, the transformation of titania into nanotubes yields materials with SSA as large as 400 m^2/g [17,22], with high pore volume and inner diameters around 7 nm, opening possibilities to disperse a larger amount of transition metal oxides or sulfides. In a recent work, we have shown that titania nanotubes can disperse efficiently 20 wt.% of WO_3 maintaining the nanotubular morphology and SSA being as high as 210 m^2/g after annealing at 400 °C [23].

Present and future trends in commercial catalysts developments for ULSD production, point out towards the increase of active phase loading from 3 Mo atoms/nm^2, for conventional catalysts, to around 5–8 atoms/nm^2 [24]. Recently, we have optimized the impregnation procedure by adjusting the pH of the Co and Mo solutions at 5.6, for samples with Mo loading of 3 atoms/nm^2 [25]. In this work, the effect of metal loading on nanotubular titania support was studied by increasing Mo content from 3 to 5 atoms/nm^2. As well, the (Co/Co + Mo) atomic ratio was optimized in samples of higher metal loading that showed high HDS activity. The influence of the nanotubular morphology of the support on the CoMoS particles was thoroughly examined by HRTEM.

2. Experimental

2.1. Synthesis of nanotubular titania

Nanotubular titania, used as support, was synthesized by a hydrothermal method, 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. The hydrothermal reaction was carried out at 100 °C, for 24 h under autogenous pressure and stirring. Thereafter, the white slurry was filtered and neutralized with a 1 M solution of nitric acid (HNO_3) overnight. Then, the material was washed with deionized water and dried at 110 °C yielding a hydrous titania powder with nanotubular morphology.

2.2. Catalysts preparation

CoMo-based catalysts were prepared by incipient wetness impregnation in two steps. In the first step, nanotubular titania (NT) was put in contact with an aqueous ammonium heptamolybdate (AHM) solution at pH 5.6 in order to have 3, 4 and 5 Mo atoms/nm^2, as indicated in Table 1. In the second step and after drying at 110 °C, Co (through a cobalt acetate aqueous solution) was impregnated on the Mo-containing samples. After impregnation, further processing included drying at 120 °C and annealing at 380 °C under air flow. Samples were labeled as NT-*x*-*y*, where NT stands for nanotubular titania support, "*x*" being the nominal amount of Mo atoms/nm^2 and "*y*" being the Co/(Co + Mo) atomic ratio. Catalysts sulfidation was carried out on oxidized samples at 380 °C, under a 10 vol.% H_2S/H_2 flow for 2 h. This step was carried out in a Pyrex glass tubular down-flow reactor, the H_2S/H_2 mixture being fed at a ~24 L/h g constant flow rate. This routine could be considered as standard in activating HDS catalysts [9,12].

2.3. HDS catalytic test

Sulfided catalysts (~0.2 g) were tested in HDS of dibenzothiophene (DBT, ~0.3 g), model molecule representing S-bearing compounds in middle distillates, in a SS316 batch reactor using *n*-hexadecane (100 ml) as solvent (initial DBT concentration 16.3 μmol/L, 674 ppm S). The reaction temperature was fixed at 320 °C and stirring rate of 1000 rpm. After operating temperature was attained, pure H_2 (UHP) was fed to the reactor to attain 56 kg/cm^2 (total pressure). Samples of liquid product were analyzed in a Varian 3400 CX gas chromatograph, equipped with a flame ionization detector and a dimethylpolysiloxane (50 m × 0.2 mm × 0.5 μm) capillary column. HDS kinetic constants were calculated assuming pseudo-first order kinetics referred to DBT concentration (*x* = conversion, *t* = time), taking into account that hydrogen was fed in such excess that its partial pressure could be considered constant:

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

k values for various catalysts were normalized by considering reaction volume and mass of catalyst used (k in $m^3/(kg_{cat}\ s)$). Even though a Langmuir–Hinshelwood protocol could provide important information about reaction kinetics, and that comparing HDS catalysts performance through a pseudo-first order kinetic model could be considered an oversimplification, the later has been recognized as a reliable method in discriminating among various HDS catalytic formulations [12,15].

2.4. Catalysts characterization

Chemical composition of the impregnated materials after annealing at 380 °C was determined by atomic absorption spectroscopy (AAS) in a PerkinElmer 2380 apparatus.

Textural properties were measured in an ASAP-2000 analyzer from Micromeritics. SSA was calculated from N_2 physisorption at −196 °C using the Brunauer–Emmet–Teller (BET) equation. Average pore size was obtained by the Barrett–Joyner–Halenda (BJH) method in the desorption stage. Materials calcined ex situ at 380 °C, were outgassed at 350 °C prior to measurements.

Raman spectra were obtained using a Yvon Jobin Horiba (T64000) spectrometer, equipped with a CCD camera detector. As a source of excitation the 514 nm line of a Spectra Physics 2018 Argon/Krypton Ion Laser system were focused through an Olympus BX41 microscope equipped with a 100× magnification objective. The laser power never exceeded 5 mW on the sample.

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed both in a JEM-2200FS microscope with accelerating voltage of 200 kV. The microscope is equipped with a Schottky-type field emission gun and an ultra high resolution configuration (Cs = 0.5 mm;

Table 1
Nominal and real chemical compositions of catalysts.

Catalysts	Mo_{nom} (atoms/nm^2)	Co/(Co + Mo)$_{nom}$ (atomic ratio)	Mo_{real} (wt.%)	Co_{real} (wt.%)	Mo_{real} (atoms/nm^2)	Co/(Co + Mo)$_{real}$ (atomic ratio)
NT-3-0.3	3	0.3	12.83	3.13	3.52	0.28
NT-4-0.3	4	0.3	13.50	4.73	3.98	0.36
NT-5-0.3	5	0.3	14.98	4.42	4.60	0.32
NT-5-0.2	5	0.2	15.14	3.23	5.03	0.26
NT-5-0.4	5	0.4	15.40	7.2	5.68	0.43