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FT-IR study of NO adsorption on MoS_2/Al_2O_3 hydrodesulfurization catalysts: Effect of catalyst preparation

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ABSTRACT

The effect of catalyst preparation on structure and performance of MoS_2/Al_2O_3 hydrodesulfurization (HDS) catalysts was studied by NO adsorption, monitored by infrared spectroscopy (NO-IR) and complemented with EXAFS. The main bands at 1785 cm^{-1} and 1690 cm^{-1} were assigned to the ν(N—O) stretching vibrations of coupled mono- or dinitrosyl surface complexes. NO adsorption on sulfided catalysts prepared with nitrilotriacetic acid (NTA) or citric acid (CA) gave rise to additional bands in the IR spectra at 1655 cm^{-1}, 1630 cm^{-1} and 1615 cm^{-1}, assigned to mononitrosyl adsorption modes. Catalysts prepared with NTA and CA were more active in thiophene HDS than calcined or dried catalysts, despite comparable NO uptake (0.10-0.12 NO/Mo). This was attributed to a changed MoS_2 edge structure as suggested by the NO-IR data, as well as to an improved degree of sulfidation as observed by EXAFS. Correlating NO uptake with MoS_2 dispersion shows that not more than 30–40% of edge and corner sites were probed with NO. This implies that only a small portion of edge sites may act as active sites in HDS catalysis.

1. Introduction

The catalytic removal of sulfur and other heteroatoms from oil distillates is an important step in the production of clean transportation fuels. Hydrodesulfurization (HDS) catalysts typically consist of molybdenum disulfide nanoparticles, promoted by cobalt or nickel, dispersed on a porous γ–alumina carrier [1]. Two types of phases may exist; a type I phase which is not fully sulfided and a fully sulfided type II phase with higher intrinsic activity [2]. The type II phase may be obtained by high temperature sulfidation or by adding chelating molecules during catalyst preparation [3]. HDS reactions are catalyzed on coordinative unsaturated sites (CUS) located at the MoS_2 edge, while the basal planes are believed to be inert [4]. Consequently, elucidation of the structure of the active edge sites and their quantification are crucial to understand HDS catalyst performance, guiding improved catalyst design.

Tunneling microscopy and electron microscopy studies with well-defined MoS_2 nanoparticles supported on Au(111) or graphite show that MoS_2 exposes molybdenum and sulfur terminated edges (Mo-edge and S-edge, respectively) [5,6]. The surface free energy of these edges is an important parameter that determines the overall shape of the MoS_2 particles [7]. The structure and distribution of specific edge sites may depend on the H_2/H_2S atmosphere, as predicted by DFT calculations [8,9], as well as preparation conditions and support interaction [4,10].

The edge structure in alumina-supported industrial catalysts is challenging to probe by atomically resolved microscopy [6,11]. Alternatively, information may be indirectly obtained *via* the adsorption of probe molecules, monitored by infrared vibrational spectroscopy (IR). Typical probe molecules employed are NO or CO, since N—O or C—O stretching vibrations are sensitive to structural and electronic properties of the formed complexes [12–14]. Adsorption of NO on MoS_2-based HDS catalysts proceeds readily at room temperature and takes place exclusively on MoS_2 edge or corner sites [15]. As such, quantitative NO adsorption may provide valuable information about the number of exposed edge sites in HDS catalysts [16]. In addition, NO adsorption on molybdenum or cobalt promoter sites can be readily distinguished by their characteristic and well-separated bands [15], which makes NO the preferred probe to study promoted catalysts.

CO was found to be a suitable probe to study the structure of unpromoted MoS_2 catalysts. Adsorption to the Mo- and S-edges may be discriminated by their C—O stretching frequencies as calculated by DFT [17], although experimental band assignment is still subject to debate [18,19]. The ratio of specific ν(C—O) bands in the

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IR spectra was found to depend on catalyst preparation conditions. Chen et al. reported that citric acid (CA) addition [20] and a higher sulfidation temperature [21] increase the ratio of S- to Mo-edge sites. They proposed that the S-edge is intrinsically more active than the Mo-edge, which may explain the beneficial effect of CA addition on catalytic activity. NO adsorption modes were also calculated to depend on Mo- and S-edge adsorption sites [22], although experimental evidence is lacking so far.

In this work we have studied MoS_2/Al_2O_3 catalytic sites by titration with NO, monitored with IR spectroscopy. The combination of quantitative and qualitative information obtained from these experiments allowed us to reassess and expand on experimental band assignments reported in literature. Catalysts with a varying degree of metal-support interaction were prepared by using nitrilotriacetic acid (NTA) and citric acid (CA) as additives. These catalysts were characterized by extended X-ray absorption fine structure (EXAFS), NO adsorption monitored by FT-IR (NO-IR) and their activity was evaluated in the HDS of thiophene.

2. Experimental

Catalysts were prepared by incipient wetness impregnation of a γ-alumina (300 m^2/g) 75–125 μm sieve fraction as described in [3,23]. Briefly, γ-alumina was impregnated with ammoniacal solutions of ammonium heptamolybdate (Sigma-Aldrich) and, if indicated, nitrilotriacetic acid (Merck) or citric acid (Sigma-Aldrich). Part of the dried (110 °C) catalyst precursor without additives (Mo^{dr}) was calcined at 450 °C (Mo^{cal}), whereas precursors prepared with NTA (Mo-NTA) or CA (Mo-CA) were not calcined. The targeted final composition of the catalysts was 4.0 at/nm^2 molybdenum loading (corresponding to 14.5 wt% after calcination), a NTA:Mo ratio of 1.0 and a CA:Mo ratio of 1.2.

Infrared spectra were measured on a Nicolet FT-IR spectrometer equipped with a cryogenic MCT detector. Self-supporting wafers (~7.5 mg/cm^2) were pressed and sulfided in a homemade *in situ* cell equipped with CaF_2 windows. Sulfidation was carried out in 1 atm H_2/H_2S(10%) (40 mL/min) at 350 °C for 2 h (6 °C/min with no additives, 2 °C/min with additives). Afterwards, the wafer was cooled to room temperature, flushed with N_2 and evacuated. The wafer was then heated again to 350 °C for 1 h (6 °C/min) and evacuated overnight. NO was passed through a liquid N_2/1-propanol cold trap and introduced stepwise into the cell *via* a calibrated sample loop connected to a pressure gauge. A spectrum was recorded after each aliquot (256 scans with a resolution of 4 cm^{-1}) up to an equilibrium pressure of 1 mbar NO. Spectra were normalized to the pellet mass of the oxidic precursor (7.5 mg/cm^2), excluding the mass of the organic additives (NTA or CA). Second derivatives were calculated with a Savitzky-Golay function (8 points).

Extended X-ray absorption fine structure (EXAFS) spectra were collected at the Mo K-edge (20.0 keV) in transmission mode at BM26A of ESRF. Sulfided samples were mounted in the glovebox as self-supporting wafers ($\mu x \approx 1.5$) and sealed with Kapton tape to prevent contact with air. The energy was selected with a Si(111) monochromator and calibrated with molybdenum foil (E_0 = 20000 eV). EXAFS spectra were background-subtracted with the Athena program and fitted with the Artemis program, which are interfaces to the IFEFFIT software package [24]. Scattering paths were calculated by FEFF6 from relevant crystal structures obtained from the ICSD database. Fitted parameters were the energy shift (ΔE_0), coordination number (CN), change in bond distance (ΔR), and the relative mean square displacement (σ^2). The amplitude reduction factor ($S_0{}^2$) was fixed at 0.98, as determined by fitting a MoS_2 reference. Fits were performed in R-space on k^1-, k^2-, and k^3-weighted spectra with a fit range of Δk = 4–16 $Å^{-1}$ and ΔR = 1–4 Å.

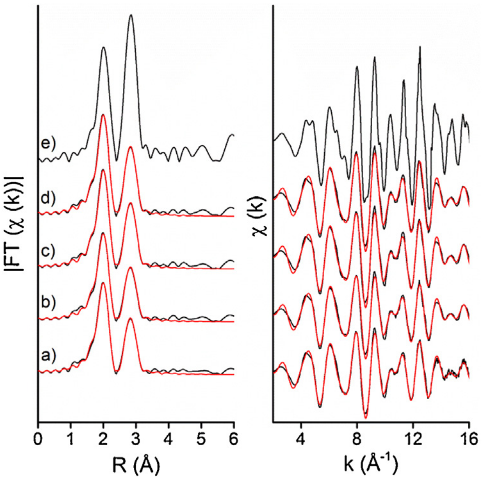

Fig. 1. Mo K-edge EXAFS spectra plotted as magnitude of the Fourier transform (left) and χ(k) (right) of Mo^{dr} (a), Mo^{cal} (b), Mo-NTA (c), Mo-CA (d) and MoS_2 (e). Spectra are plotted with a k-weight of 3. Black lines represent experimental data and red lines fitted spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Thiophene activity tests were done in a flow reactor at atmospheric pressure under differential conditions. Approximately 100 mg of precisely weighted 75–125 μm catalyst particles, diluted with 200 mg SiC (250 μm), were sulfided in 60 mL/min H_2/H_2S(10%) at 350 °C for 2 h. Then, the feed was switched to 4% (v/v) thiophene (Sigma-Aldrich) diluted in H_2 at a flow rate of 100 mL/min. The reaction was run at 400 °C for 13 h, afterwards the temperature was decreased to 350 °C and steady-state activity was measured under differential conditions over a period of 4 h by gas chromatography coupled with flame ionization detection (GC-FID). The reaction rate (r_{Thio}), normalized per gram of Mo, was calculated according to:

$$r_{Thio} = \left(\frac{F_{Thio}}{m_{cat} w_{Mo}}\right) X$$

where F_{Thio} is the flow of thiophene [mol_{Thio} h^{-1}], m_{cat} the catalyst mass [kg], w_{Mo} the fraction of molybdenum [kg_{Mo} $kg_{cat}{}^{-1}$], and X the conversion. The experimental uncertainty in the reaction rate was ± 5%.

3. Results and discussion

3.1. EXAFS analysis

Fig. 1 shows Mo-K edge EXAFS spectra of the MoS_2/Al_2O_3 catalysts and a bulk MoS_2 reference. Spectra of the supported catalysts are in good agreement with that of bulk MoS_2. The first coordination shell (2.0 Å, not phase corrected) in the Fourier transform (FT) is assigned to Mo-S contributions and the second coordination shell (2.8 Å, not phase corrected) is assigned to Mo–Mo contributions. It is evident that the amplitude of the second coordination shell of the samples is lower than that of bulk MoS_2 (Mo–Mo CN = 6), which is typical of nanoparticulate MoS_2 [25].

Table 1 reports the EXAFS fit results of the samples. The Mo-S coordination number (CN) of the dried and calcined catalyst is 5.5, lower than the value of bulk MoS_2 (CN = 6), indicating that the catalysts are not fully sulfided. The degrees of sulfidation of Mo-NTA and Mo-CA were comparable and slightly higher as indicated by their Mo-S CN (5.7–5.8), which suggests that NTA and CA addition had a similar effect on the structure of sulfided catalysts. The slightly higher sulfidation degree obtained after NTA and CA addition may be attributed to reduced metal-support interaction in agreement

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