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Effect of high pressure sulfidation on the morphology and reactivity of MoS_2 slabs on MoS_2/Al_2O_3 catalyst prepared with citric acid

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ABSTRACT

MoS_2/Al_2O_3 catalysts were prepared by a simultaneous impregnation method with citric acid as chelating agent in order to investigate the effect of high pressure sulfidation on the morphology and reactivity of MoS_2 slabs by infrared spectroscopy of CO adsorption (IR/CO), transmission electron microscopy, thiophene hydrodesulfurization (HDS) and 2,6-dimethylaniline hydrodenitrogenation (HDN) reactions. It is found that the MoS_2 slabs are more truncated when sulfided at higher pressure, exposing larger S-edge/M-edge ratio. The thiophene HDS activity of MoS_2/Al_2O_3 catalysts was significantly improved by high pressure sulfidation. The MoS_2 edges formed after high pressure sulfidation are very stable toward H_2-treatment, while the same H_2-treatment can create sulfur vacancies on both M-edge and S-edge of the 0.1 MPa sulfided MoS_2 slabs. Meanwhile, parallel between the IR/CO results and HDN test suggests that the S-edge favors the C–N bond scission whereas the M-edge benefits the hydrogenation in HDN reaction.

1. Introduction

Co (or Ni)-promoted MoS_2/Al_2O_3 catalysts are among the most used hydrotreating catalysts in refineries [1]. The structure of this type of catalysts is generally described by the so-called Co(Ni)MoS model [2], in which the Co (or Ni) promoters decorate the edges of MoS_2 slabs to form the catalytic active sites. In order to well understand the decoration effect of promoters (also known as the synergetic effect between Co(or Ni) and MoS_2 slabs), the fundamental investigation on the edges exposed by MoS_2 slabs under different conditions, i.e. the MoS_2 morphology, is of great importance [3].

The MoS_2 slabs expose principally two types of edges: the Mo terminated edge (M-edge) and the sulfur terminated edge (S-edge) [4]. The relative concentrations of these two edges give different MoS_2 morphologies. Although it is predicted by density functional theory (DFT) calculations that the MoS_2 slabs will adopt different morphologies under different sulfidation and preparation conditions [5,6], approaches that could experimentally depict such morphologies on *real type Al_2O_3-supported catalyst* are still scarce. As a proven technique, low temperature CO adsorption followed by IR spectroscopy (IR/CO) has been employed to characterize the Al_2O_3-supported sulfide catalysts since 1980s [7,8], and the obtained edge site concentration correlated well with the thiophene HDS activity data [9]. On MoS_2 phase, two CO adsorption bands located at around 2110 and 2065 cm^{-1} were observed, but no consensus could be reached on their assignment for a long time [8,10–12]. Recently, we clarified this assignment [13], by analyzing the data obtained by IR/CO, high resolution TEM, isotopic CO adsorption, and DFT calculations, showing that only the M-edge/S-edge assignment is coherent with the different experimental results, whereas other assignments such as edge/corner, carbide/sulfide or variation in slab stacking are in contradiction with at least one experimental data. Accordingly, the ν(CO) bands located at ~2110 and ~2065 cm^{-1} are respectively attributed to CO adsorption on the M-edge and S-edge of MoS_2 slabs [10,12]. Based on this assignment, we demonstrated that the morphology of Al_2O_3-supported MoS_2 slabs can be tuned from a slightly truncated triangle exposing mainly M-edge to a hexagonal shape with both M-edge and S-edge by varying sulfidation and preparation conditions [13–15]. These IR/CO results agree well with those obtained on model catalyst [3] and by DFT predictions [5,6]. The IR/CO method is thus revealed as one of the few approaches that could depict the MoS_2 morphology on *real type* catalysts.

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In this work, we extend our previous studies to investigate the effect of high pressure sulfidation on MoS_2 morphology on MoS_2/Al_2O_3 catalyst. Such study is of great interest because the catalyst sulfidation for industrial applications was generally carried out at high pressure (3–5 MPa) whereas in most academic studies the catalysts were sulfided at atmospheric pressure [1]. Thus, the effect of sulfidation pressure should be examined in detail to get more relevant structure–activity relationship. For this purpose, a specific IR cell called CellEx was recently developed, which allows to sulfide catalyst at different H_2S/H_2 pressures (0.1–4.0 MPa), and then to *in situ* characterize the sample by IR spectroscopy. In this work, we report the *in situ* IR/CO characterizations on a series of MoS_2/Al_2O_3 catalysts prepared with different amounts of citric acid (CA) and sulfided at both atmospheric (0.1 MPa) and high (4.0 MPa) pressure. To further rationalize the IR/CO characterizations, we performed high resolution TEM on both atmospheric and high pressure sulfided samples. The reactivity of M-edge and S-edge on MoS_2 is then discussed combining the IR/CO results with the catalytic hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity data.

2. Experimental

2.1. Catalyst preparation

A series of Mo/Al_2O_3 catalysts with different amounts of citric acid (CA) were prepared by a one-step pore volume impregnation method. Firstly, the impregnation solutions were prepared with different amounts of citric acid (CA, $C_6H_8O_7{\cdot}H_2O$, PROLABO) and a constant amount of ammonium heptamolybdatetetrahydrate (AHT, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, MERCK). Afterward, the γ-Al_2O_3 support (SASOL, specific surface area of 252 $m^2\,g^{-1}$ and pore volume of 0.84 $mL\,g^{-1}$) pre-calcined in air at 723 K for 2 h was added into the solutions and strongly shaken for 2 h. Finally, the catalysts were dried at 383 K for 3 h. Note that these catalysts were not calcined in order to keep the chelating agent in its initial form. Hereinafter, the Mo/Al_2O_3 catalysts prepared with citric acid are denoted as $Mo(CA/Mo = x)/Al_2O_3$. X refers to the molar ratio of citric acid (CA) to Mo. x = 0, 0.5, 1.0, and 2.0 while the Mo precursor (AHT) content was kept at 0.19 mmol per gram of Al_2O_3 support.

2.2. Infrared (IR) spectroscopy characterization

IR characterization was performed on a specifically designed setup called CellEx. The CellEx consists of three parts: (i) a stainless steel reactor for catalyst sulfidation and/or other treatment under different temperature, pressure and gas phase; (ii) an IR cell inserted in a spectrometer for spectroscopic characterization; and (iii) a transfer connection for transferring sample from reactor into IR cell under inert gas. Thus, within the CellEx, the catalysts can be treated under different conditions and sequentially *in situ* characterized by IR spectroscopy without any air pollution.

2.2.1. Catalyst sulfidation

Catalyst sulfidation was performed in the stainless reactor of CellEx. Catalyst sample was firstly grounded and pressed into self-supporting pellet of about 8 $mg\,cm^{-2}$ (precisely weighted). The pellet was introduced into the reactor that was then evacuated at room temperature down to 1.33 Pa. After that the pellet was sulfided at 0.1 MPa or 4.0 MPa with the following procedure. (i) 0.1 MPa sulfidation: firstly, a gas mixture of 0.1 MPa 30 $mL\,min^{-1}$ 10%H_2S/H_2 was introduced into the reactor. Then, the pellet was heated with a rate of 3 $K\,min^{-1}$ to 623 K and maintained at this temperature for 2 h. Sequentially, the reactor was flushed with Ar at 623 K and then cooled down to room temperature under Ar. (ii) 4.0 MPa sulfidation: the pressure in the reactor was firstly increased to 4.0 MPa with 10% H_2S/H_2 mixture. Then, the pellet was heated with a rate of 3 $K\,min^{-1}$ to 623 K and maintained at this temperature for 2 h. After that, the reactor pressure was decreased to atmospheric pressure. Sequentially, the reactor was flushed with Ar at 623 K and then cooled down to room temperature under Ar. Finally, the sulfided pellet was transferred under Ar to the IR cell for IR characterization.

2.2.2. Low-temperature CO adsorption followed by IR spectroscopy characterization (IR/CO)

Once in the IR cell, the sulfided pellet was firstly heated at 6 $K\,min^{-1}$ up to 623 K and kept for 1 h under evacuation. The final pressure in the IR cell after evacuation should reach 10^{-3} Pa. After that, the pellet was cooled down by liquid nitrogen to 100 K for CO adsorption. CO adsorption was performed by introducing in the IR cell small calibrated doses of CO (0.03–1.20 μmol of CO) and finally 133 Pa CO at equilibrium. IR spectra of adsorbed CO were recorded with a Nicolet spectrometer equipped with a MCT detector, taking 256 scans. Note that the graphical resolution is 0.5 cm^{-1}. For comparison, all the spectra presented were normalized to a pellet of 5 $mg\,cm^{-2}$ of sulfided catalyst.

The obtained IR spectra were further decomposed with Peakfit V4.12 using "Autofit peak II—Second derivative Methods". Then, the concentration of each type of MoS_2 edge sites was determined using the molar extinction coefficient of CO adsorbed on M-edge ($\varepsilon_{\text{M-edge}}$) and S-edge ($\varepsilon_{\text{S-edge}}$) previously measured ($\varepsilon_{\text{M-edge}}$ and $\varepsilon_{\text{S-edge}}$ are 20 ± 3 μmol^{-1} cm and 35 ± 9 μmol^{-1} cm, respectively [15]). Details for spectral decomposition, $\varepsilon_{\text{M-edge}}$ and $\varepsilon_{\text{S-edge}}$ measurement, and edge site concentration calculation are provided in *Supplementary Material.*

2.2.3. Catalyst sulfidation followed by H_2 treatment

Catalyst sulfidation followed by H_2 treatment was carried out in the stainless steel reactor of CellEx. The catalyst pellet was firstly sulfided at either 0.1 MPa or 4.0 MPa as described in Section 2.2.1 and then directly treated by 30 $mL\,min^{-1}$ 0.1 MPa H_2 gas for 2 h at 623 K. After this treatment, the reactor was flushed with Ar at 623 K. Then, the pellet was cooled down to room temperature under Ar and transferred to the IR cell for IR/CO characterization.

2.3. Thiophene hydrodesulfurization (HDS) test

Thiophene HDS test was performed in a stainless steel reactor (Sotelem). First, the catalyst was sulfided at 623 K with a 10% H_2S/H_2 at 0.1 MPa or 4.0 MPa following the same sulfidation procedure as for IR characterization (Section 2.2.1). Then thiophene HDS test was carried out at 623 K and 0.1 MPa with around (but precisely weighted) 50 mg of sulfided catalyst. Thiophene was introduced into the reactor by passing 70 $mL\,min^{-1}$ of H_2 flow through a thiophene saturator maintained at 291 K and mixed with a flow of 20 $mL\,min^{-1}$ 10% H_2S/H_2. The partial pressures of thiophene, H_2 and H_2S in the mixture are 8 kPa, 91.2 kPa, and 2.1 kPa, respectively. After 24 h reaction, the outlet gas was analyzed by a Varian 3900 chromatograph equipped with flame ionization (FID) detector. The concentrations of butane, 1-butene, trans-2-butene, cis-2-butene, tetrahydrothiophene (THT), as well as thiophene were recorded. The reaction rate was calculated as $r_{\text{HDS}} = (F/m) * X$, where F/m is the molar flow rate of thiophene per gram of catalyst and X is the thiophene HDS conversion which is below 5%.

2.4. 2,6-Dimethylaniline (2,6-DMA) hydrodenitrogenation (HDN) test

The 2,6-DMA HDN activity test was performed in a stainless steel reactor (Sotelem). About 300 mg of catalyst was sulfided