Journal of Molecular Catalysis A: Chemical 309 (2009) 79–88

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Relation between sulfur coordination of active sites and HDS activity for Mo and NiMo catalysts

Bas M. Vogelaar[a,*], Narinobu Kagami[b], Thomas F. van der Zijden[a], A. Dick van Langeveld[a], Sonja Eijsbouts[c], Jacob A. Moulijn[a]

[a] *Delft University of Technology, Faculty of Applied Sciences, Department of Reactor and Catalysis Engineering, Julianalaan 136, 2628 BL Delft, The Netherlands*
[b] *Idemitzu Kosan Co. Ltd., 26 Anesakikaigan Ichihara-city, Chiba 229-0107, Japan*
[c] *Albemarle Catalysts, P.O. Box 37650, 1030 BE Amsterdam, The Netherlands*

ARTICLE INFO

Article history:
Received 13 December 2008
Received in revised form 21 April 2009
Accepted 25 April 2009
Available online 3 May 2009

Keywords:
Hydrodesulfurization
Molybdenum sulfide
Active phase
CO adsorption
Infrared spectroscopy

ABSTRACT

The structure of sulfidic Type I and Type II Mo and NiMo alumina supported hydrodesulfurization (HDS) catalysts was studied using infrared (IR) analysis of adsorbed CO. The results were compared to the catalytic activity in gas phase thiophene and liquid phase dibenzothiophene HDS reactions. IR analysis confirmed the presence of MoS_2- and NiMoS-type phases. The Type II NiMo catalyst (prepared using NTA as chelating agent) had a fully promoted edge structure, whereas the Type I (calcined) NiMo catalyst exhibited both promoted and unpromoted edge sites, confirming that NTA enhances the Ni-decoration of the MoS_2 edges. The active phase in both types of catalysts exhibited a dynamic and reversible behavior in terms of sulfur coordination. The catalysts exposed a higher number and/or a higher degree of coordinative unsaturation of vacant sites under gas phase thiophene HDS conditions than directly after sulfidation. The NiMo catalysts could be fully restored to their initial state by resulfiding after thiophene HDS, whereas some sites of the Mo catalysts were irreversibly blocked. Apparently, the NiMo catalysts were able to suppress coke deposition on the active sites under the conditions applied, in contrast to the Mo catalysts. An inverse correlation was found between the gas phase thiophene HDS conversion and the number of vacant sites present on the catalyst surface. A similar trend was observed for the ratio between hydrogenation and direct desulfurization of dibenzothiophene in the liquid phase HDS reaction. These correlations show that the thiophene HDS reaction and the dibenzothiophene hydrogenation pathway are catalyzed by sulfided species on the active phase, while the direct desulfurization pathway is catalyzed by vacant sites.

1. Introduction

CoMo and NiMo based hydrodesulfurization (HDS) catalysts have been used in industrial hydrotreating processes for decades [1]. Although many improvements have been made in the composition, metal dispersion and support material of these catalysts, their formulation has basically remained unchanged. In order to further improve these catalysts, fundamental insights in the structure of these catalysts and the nature of the active sites are needed. Although great progress has been made over the years, crucial details regarding the structure of this type of catalysts on the atomic scale have not been fully uncovered. The observation of unpromoted and promoted MoS_2 slabs under the STM microscope [2,3] inspired several research groups to perform new modeling studies on the edge structure of MoS_2 slabs in HDS catalysts, see e.g. [4–6]. Comprehensive reviews on this topic were published by Raybaud [7] and Sun et al. [8]. An example of different edge configurations for a MoS_2 slab is shown in Fig. 1. The coordination number or degree of coordinative unsaturation of the edge Mo atoms changes as a function of sulfur content [3]. Sulfur atoms on the edges of the active phase can be removed by reacting with hydrogen, yielding coordinatively unsaturated (cus) Mo sites. The case of promoted HDS catalysts is more complex [9]. Most researchers have accepted the CoMoS/NiMoS model, in which the promoter atoms are atomically dispersed over the MoS_2 edges, forming the so-called CoMoS or NiMoS phase. In this model the promoter atoms are either the active centers or able to enhance (promote) the activity of the MoS_2 edge sites [1]. It has been well established that at least two different types of active sites are involved in HDS reactions and it is generally believed that vacant (cus) sites are responsible for the removal of hetero-atoms [1]. Furthermore, several researchers propose that fully sulfided species (i.e. sulfur that is a part of the catalyst active phase) may play a role in the HDS reaction [10–13]. These sugges-

---

[*] Corresponding author. Current address: Albemarle Catalysts, P.O. Box 37650, 1030 BE Amsterdam, The Netherlands. Tel.: +31 20 6347648; fax: +31 20 6347653.
E-mail address: Bas.Vogelaar@albemarle.com (B.M. Vogelaar).

1381-1169/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2009.04.018

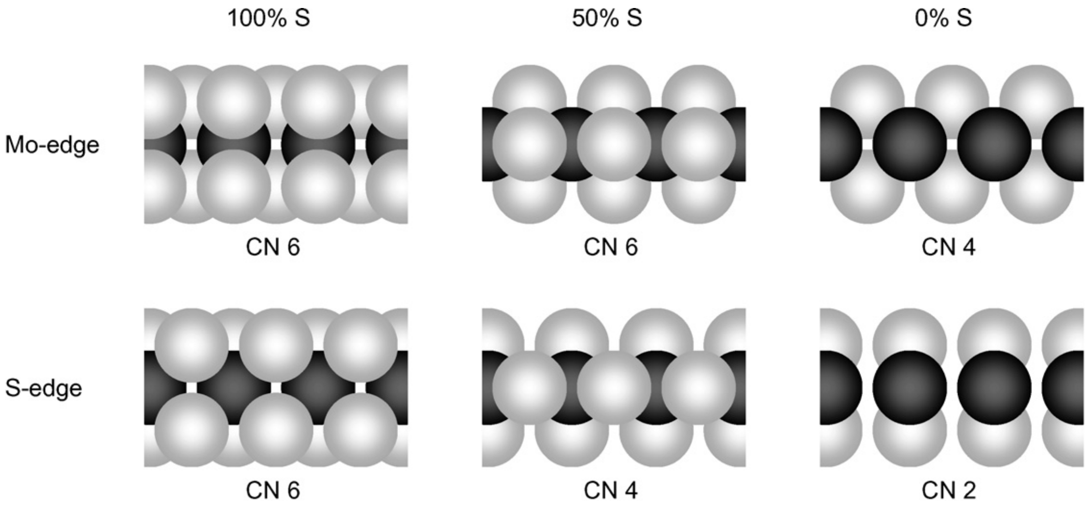

Fig. 1. Ball model (side view) of the edges of a MoS_2 slab at different sulfur loadings, adapted from Ref. [3]. Dark spheres represent Mo, light spheres S atoms. Indicated are the total sulfur coordination (%) of the edge and the coordination number (CN) for Mo in each case.

tions are mostly based on the observed selectivity of the catalyst, which was recently reported again for the HDS of dibenzothiophene [14].

In the present study, the active phase of Mo and NiMo based HDS catalysts was characterized using infrared (IR) analysis of adsorbed CO. Furthermore, these results were correlated to the thiophene and dibenzothiophene HDS activity of the different catalysts. The adsorption of probe molecules like CO, coupled with vibrational spectroscopy is a widely used and powerful tool for the identification of the surface structure and properties of various inorganic materials, including HDS catalysts [15–17]. Adsorbed CO molecules interact with transition metals through their molecular orbitals, which affects the CO bond strength. The resulting CO bond stretching frequency observed in the IR spectrum is a function of the type of metal on which it adsorbs, the oxidation state of the metal and the coordination number of the metal center. For this study, Mo and NiMo based catalysts were used with different morphologies (so-called Type I and Type II). It is generally believed that the Type II active phase has improved properties, resulting in a higher HDS activity (e.g. see [18–20]). Dried Type II catalysts were prepared using nitrilo triacetic acid (NTA) as a complexing agent and calcined Type I catalysts were prepared without NTA. The catalysts were subjected to various treatments including HDS reactions, in order to gain further insight in the active phase structure and its catalytic function.

2. Experimental

2.1. Catalysts

Four different catalysts were prepared, as summarized in Table 1. A solution of ammonium dimolybdate $(NH_4)_2Mo_2O_7$ and nickel nitrate $Ni(NO_3)_2$ was impregnated onto 1.5 mm cylindrical extrudates of a high purity γ-Al_2O_3 support (Ketjen CK 300). The resulting catalysts were dried at 393 K for 1 h and calcined at 723 K for 1 h (heating rate 5 K/min). This procedure leads to the formation of typical Type I HDS catalysts. Their so-called Type II counterparts were prepared using a different procedure. Nitrilo triacetic acid (NTA) was added to the impregnating solution as a chelating agent, with a ratio of 1.2 mol NTA per mol Mo (i.e. 2.4 mol NTA per mol Ni). The resulting catalysts were dried at 393 K for 1 h and not calcined. Note that for measuring the catalyst properties (Table 1), all catalysts were calcined. After preparation, the catalyst extrudates were crushed and sieved to obtain a particle fraction of 75–125 μm diameter for the activity tests and a fraction <75 μm diameter for the IR analyses. The following gas phase sulfiding procedure was used: the catalyst was exposed to a mixture of 5 vol% H_2S and 50 vol% H_2 in Ar. The temperature was held at 298 K for 0.5 h, increased with 10 K/min to 673 K and held for 2 h at 673 K. A lower heating rate of 2 K/min was applied for the sulfiding of the NTA based catalysts, to ensure the homogeneous decomposition of the chelating agent. Throughout this work, Type I catalysts are indicated as Mo and NiMo, while Type II catalysts are indicated as Mo(NTA) and NiMo(NTA).

2.2. IR analysis of adsorbed CO

A dedicated infrared in situ analysis setup (IRIS) was used for this study, as described in [20]. About 20 mg of the crushed catalyst (<75 μm) was pressed into a self-supporting disk by applying a pressure of 0.5 GPa for 1 min. The NiMo catalysts were diluted with an equal weight of the γ-Al_2O_3 support material, before pressing, to enhance the transparency of the samples. Inside the IRIS equipment, the sample could be transported between the "high temperature chamber" (HTC) for pretreatment and the "infrared chamber" (IRC) for analysis, without exposure to air. Several pretreatment procedures were carried out; sulfiding (using the procedure described in Section 2.1), treatment in H_2 and thiophene HDS in a mixture of 4.3 vol% thiophene in H_2. During pretreatment in the HTC, the sample was subjected to a gas stream of

Table 1
Properties of the prepared catalysts.

Catalyst	Mo loading (wt% MoO_3)	Ni loading (wt% NiO)	Pore volume (cm^3/g)	Surface area (m^2/g)
Mo	10.25	–	0.58	274
Mo(NTA)	10.12	–	0.58	272
NiMo	10.04	2.44	0.56	268
NiMo(NTA)	9.93	2.37	0.56	265

Analysis data were provided by Albemarle Catalysts. Catalyst properties were measured after calcination.