Magnesia-supported Mo, CoMo and NiMo sulfide catalysts prepared by nonaqueous impregnation: parallel HDS/HDN of thiophene and pyridine and TEM microstructure

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MgO-supported Mo, CoMo and NiMo sulfide catalysts were prepared by impregnation using slurry MoO_3/methanol and solutions of Ni and Co nitrates in methanol. The catalysts exhibited very high hydrodesulfurization activity and low hydrodenitrogenation activity in competitive reactions of thiophene and pyridine. The promotion effect for HDS of Ni and Co was higher for our MgO-supported MoS_2 catalysts than for conventional Al_2O_3-supported catalysts. The specific features in the TEM images of MgO-supported catalysts as compared to conventional Al_2O_3-supported catalysts were fairly broad MoS_2 slab length distribution and the presence of unusually long MoS_2 slabs.

KEY WORDS: sulfide catalysts; MgO support; hydrodesulfurization; hydrodenitrogenation; TEM/HREM.

1. Introduction

Removal of sulfur- and nitrogen-containing compounds by catalytic hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are important reactions in the processing of petroleum feedstocks. The catalysts used are Mo, CoMo and NiMo sulfides supported on Al_2O_3 [1–3]. The driving force for further research on improvement of these catalysts is mainly connected with environmental aspects (e.g., [4]). One important direction of this research focuses on the support material for the active sulfides. Activated carbon, TiO_2, ZrO_2, zeolites, MgO and various mixed oxides have been studied as potential alternatives for the conventional Al_2O_3 support [5–8].

Basic MgO (isoelectric point of about 12) forms a class apart from other supports, which are acidic or neutral. Its basicity might be favorable because of increased interaction between acidic Mo species (MoO_3 in the catalyst precursor and Lewis acidity of MoS_2 edges), leading to and stabilizing high dispersion of the active phase. Additionally, acidic supports promote coke formation on the surface of working catalysts, which decreases steady state catalytic activity [9]. Reduced coke formation is expected for basic support materials.

The few research groups publishing on Mo-based MgO-supported catalysts have used preparation methods similar to what is used for conventional alumina-supported catalysts [10–14]. These involve aqueous impregnation with ammonium heptamolybdate and cobalt or nickel nitrate followed by calcination at 450–500 °C. However, this procedure does not take into account that MgO reacts easily to form $Mg(OH)_2$ during aqueous impregnation and subsequent drying, and that MgO is partially dissolved at the natural pH of the impregnation solutions. Furthermore, Co(Ni) tends to penetrate into the bulk of MgO forming a solid Co(Ni)O/MgO solution during long calcination procedures above 400 °C. In our opinion, these facts explain the low HDS activity of the Co(Ni)Mo/MgO sulfide catalysts reported by previous authors as compared to the corresponding conventional Al_2O_3-supported catalysts.

We have reported recently that very active MgO-supported Mo and Co(Ni)Mo sulfide HDS catalysts can be obtained by impregnation using methanol instead of water as the solvent, followed by short calcination at the low temperature of 350 °C (Mo/MgO [15], Co(Ni)Mo/MgO [16]). High surface area MgO is chemically and texturally stable in methanol, and mild calcination prevents the formation of Co(Ni)O/MgO solid solution. The Mo/MgO was prepared by the reaction of MgO with the slurry of MoO_3 in methanol containing 4 wt% of water [15]. The solubility of MoO_3 is very low. However, the dissolved Mo species were chemisorbed on the MgO surface and additional MoO_3 was dissolved until all solid MoO_3 particles disappeared from the impregnation slurry. The resulting MoO_3/MgO catalyst was impregnated by a solution of Co or Ni nitrate in pure methanol [16]. The catalytic performance was compared using HDS of benzothiophene [16]. The

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present work tests these catalysts in another model reaction, competitive HDS of thiophene and HDN of pyridine. The important question of this research is whether the MgO-supported catalysts exhibit high HDS activity also in the presence of pyridine, which is known to strongly inhibit the HDS activity of Al_2O_3-supported catalysts. The HDN activity itself is also of interest, as no data on HDN over MgO-supported sulfides have been reported yet.

Transmission electron microscopy (TEM) has contributed to the present knowledge of the structure of Mo-based sulfide catalysts. TEM has shown that small slabs of the layered MoS_2 are present at the support surface (for instance, [17,18]). The length and stacking of these slabs depend on the support type, the presence of promoters Co and Ni and other additives used in catalyst preparation as well as on the sulfidation conditions. Data available on MgO-supported sulfide catalysts are very limited (see below) and concern low-activity catalysts prepared by aqueous impregnation. TEM studies on our MgO-supported catalysts are performed to study the dispersion and morphology of the (promoted) MgO-supported MoS_2 slabs.

2. Experimental

2.1. Catalyst preparation

Catalysts are denoted by xNi(Co)yMo/MgO, x being the content of NiO or CoO in wt% and y that of MoO_3 in wt%. The preparation of the MgO-supported catalysts is described in detail in [15,16]. The MoO_3/MgO catalyst was prepared by the reaction of high surface area MgO (BET surface area of 243 $m^2\,g^{-1}$) with the slurry of MoO_3 in aqueous methanol (4 wt% of water) and drying in a rotary vacuum evaporator at 100 °C (no calcination). CoO and NiO were deposited onto the MoO_3/MgO by impregnation using solutions of the corresponding nitrates in methanol, followed by calcination for 40 min in airflow at 350 °C. The high surface area of the MgO support was preserved during this preparation procedure, and the surface area of the resulting catalyst precursors was in the range of 220–255 $m^2\,g^{-1}$.

Commercial 15Mo/Al_2O_3 (BASF M8–30), 3.5Co15Mo/Al_2O_3 (Shell 344) and 3.5Ni19Mo/Al_2O_3 (Shell 324) samples were used as reference catalysts for the activity measurements.

2.2. Catalytic activity measurements

Competitive thiophene HDS and pyridine HDN experiments were performed in a flow system with a fixed bed of catalyst and with all reactants in the gas phase. The i.d. of the reactor was 2 mm and the catalyst particle size fraction was 0.16–0.32 mm. The composition of the inlet and outlet streams of the reactor was determined using on-line GC (2.5-m glass column of i.d. 3 mm packed with 60/80 Carbopack B/4% Carbowax 20 M/0.8% KOH (Supelco) at 122 °C). The flow of pyridine, F_{PY}, thiophene, F_{TH} and hydrogen, F_{H_2} was 0.088, 0.096, and 400 $mmol\,h^{-1}$, respectively. The pressure was 2 MPa and the temperature was 320 °C. The space time W/F was varied using various catalyst charges W (10–100 mg) in such a way that the conversion of thiophene varied between 0 and 100%. The catalysts were presulfided *ex situ* (flow of 1:10 H_2S/H_2 mixture with a temperature ramp of 6 °C/ min from room temperature to 400 °C and a dwell time of 1 h at 400 °C) and stored in an airtight vial. In each kinetic run, the catalyst was sulfided once more *in situ* under the same conditions as used for the *ex situ* presulfidation. The products of thiophene (TH) HDS were C_4 hydrocarbons (C4) and hydrogen sulfide. The products of pyridine (PY) HDN were piperidine (PI), pentylamine (PA), C_5 hydrocarbons (C5) and ammonia. SA (saturated amines) denotes the sum of PI and PA. The conversions were defined as follows: conversion of TH, $x_{TH} = n^\circ_{TH} - n_{TH}/n^\circ_{TH}$, overall conversion of PY, $x_{PY} = n^\circ_{PY} - n_{PY}/n^\circ_{PY}$, conversion of PY to SA, $x_{SA} = n_{SA}/n^\circ_{PY}$ and conversion of PY to C5, $x_{C5} = n_{C5}/n^\circ_{PY}$, where n and n° are the final and initial number of moles, respectively.

2.3. Transmission electron microscopy

TEM was performed using a Philips CM30UT electron microscope with a field emission gun as the source of electrons operated at 300 kV. The samples were presulfided in a flow of 1:10 H_2S/H_2 using the following sequence of operations: 30 min at room temperature in H_2S/H_2 flow, temperature ramp program of 8.4 °C min^{-1} to 400 °C in H_2S/H_2 flow, dwell time of 100 min at 400 °C in H_2S/H_2 flow, temperature ramp of 6.7 °C from 400 to 300 °C in H_2S/H_2 flow, H_2S/H_2 flow replaced by N_2 flow at 300 °C, dwell time of 20 min in N_2 flow, cooling to room temperature in N_2 flow in 25 min and transfer to gas-tight vial under N_2 flow. The sulfided samples were mounted on a Quantifoil® microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in n-hexane on the grid, followed by drying at ambient conditions, all in an Ar glove box. The samples were transferred to the microscope in a special vacuum-transfer sample holder under exclusion of air [19].

3. Results and discussion

The catalytic results obtained are illustrated by data for CoMo/MgO and CoMo/Al_2O_3 catalysts in figure 1. No intermediate was observed in TH HDS and the course of the reaction is described by reaction (1) of

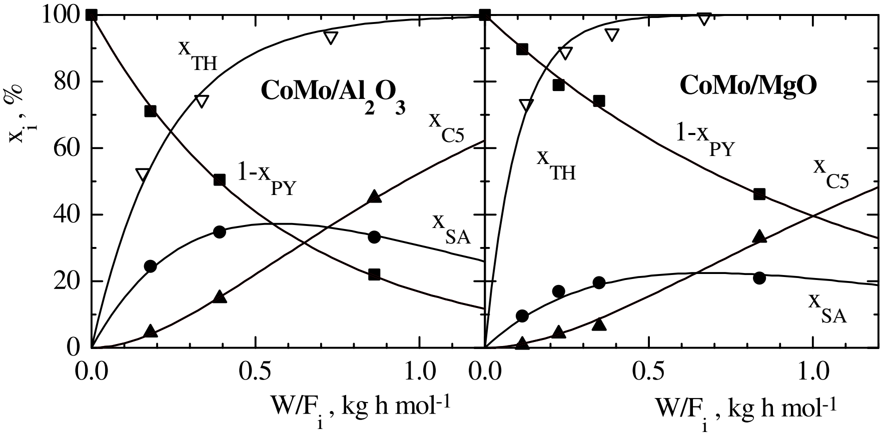

Figure 1. Parallel HDS of thiophene and HDN of pyridine over CoMo sulfide catalysts at a temperature of 320 °C and pressure of 2 MPa. HDS: x_{TH} – conversion of thiophene, HDN: $(1-x_{PY})$ – disappearance of pyridine, x_{SA} – conversion to intermediate saturated amines, x_{C5} – conversion to C_5 hydrocarbons (final product of HDN).

pseudo first-order rate kinetics with the rate constant k_1. The fit is illustrated in figure 1. The relative HDS activity of the catalyst i, $A_{HDS,TH}$, was defined as the ratio $k_{1,i}/k_{1,r}$, where r is the reference catalyst $15Mo/Al_2O_3$.

$$\mathrm{TH} \xrightarrow{H_2} \mathrm{C4} + \mathrm{H_2S} \tag{1}$$

The amount of PA was always at least one order of magnitude lower than that of PI, and the course of the PY reaction is described by the simplified reaction scheme of two consecutive irreversible reactions (2) and (3) of pseudo first-order kinetics with rate constants k_2 and k_3, respectively. The fit is illustrated in figure 1. Neither k_2 nor k_3 alone is the measure of the overall HDN activity. The relative HDN activity of the catalyst i, A_{HDN}, is defined as the ratio of space velocities at x_{C5} of 20%, $(F/W)_i/(F/W)_r$, where r is the reference catalyst $15Mo/Al_2O_3$. It was checked that the same relative activities were obtained when x_{C5} of 30% was used instead of 20%.

$$\mathrm{PY} \xrightarrow{H_2} \mathrm{SA} \tag{2}$$

$$\mathrm{SA} \xrightarrow{H_2} \mathrm{C5} + \mathrm{NH_3} \tag{3}$$

The relative HDS activities obtained in the present work are presented in table 1 together with the activities for benzothiophene HDS, $A_{HDS,BT}$, obtained previously using the same catalysts [16]. The unpromoted Mo/MgO catalyst shows activities for both HDS and HDN, which are virtually identical to those of its alumina-supported counterpart. Regardless of the support material used, promotion with Co or Ni increases HDS activity tremendously and HDN activity slightly. HDS promotion is hampered by competitive HDN, but is still significant in the competitive HDS/HDN catalytic test. Our results prove that very active HDS centers can be obtained using MgO support when the very specific chemistry of MgO (as compared with other supports) is taken into account.

The promotion effect for PY HDN has been reported to depend on the H_2S/H_2 ratio in the reaction mixture, on H_2 pressure and on reaction temperature [2]. These factors influence the ratio r_2/r_3 and thus the selectivity to saturated amines, S_{SA}. When this ratio is high (as indicated by high S_{SA}), the promotion effect is small [2]. The insignificant promotion effect for PY HDN observed for our catalysts can thus be explained by the low H_2S/H_2 ratio in our test (no H_2S in the feed), which causes a high selectivity for SA [2].

The promotion effect for competitive PY HDN for MgO-supported catalysts (table 1) seems to be somewhat smaller than that for Al_2O_3-supported catalysts. According to the above analysis, the lower promotion in HDN over MgO-supported catalysts should be accompanied by their higher S_{SA} selectivity as compared to Al_2O_3-supported catalysts. The selectivity S_{SA} was evaluated by plotting x_{SA} versus x_{PY} and presenting the ratios k_2/k_3 in figure 2. It is seen in figure 2 that the

Table 1
Relative activity of the catalysts in HDS of benzothiophene, $A_{HDS,BT}$, and in parallel HDS of thiophene, $A_{HDS,TH}$, and HDN of pyridine, A_{HDN}

Catalyst	$A_{HDS,BT}$[a]	$A_{HDS,TH}$	A_{HDN}
MgO-supported catalysts			
3.5Co	0.2	–	–
3Ni	0.1	0.1	0.1
15Mo	0.9	1.2	1.0
3.5Co15Mo	30.9	10.5	1.4
3Ni15Mo	19.8	11.0	1.6
Al_2O_3-supported catalysts			
15Mo	1.0	1.0	1.0
3.5Co15Mo	13.3	4.6	1.8
3.5Ni19Mo	13.0	9.3	3.4

[a] Data from T. Klicpera and M. Zdražil, J. Catal. 206 (2002) 314 [16].

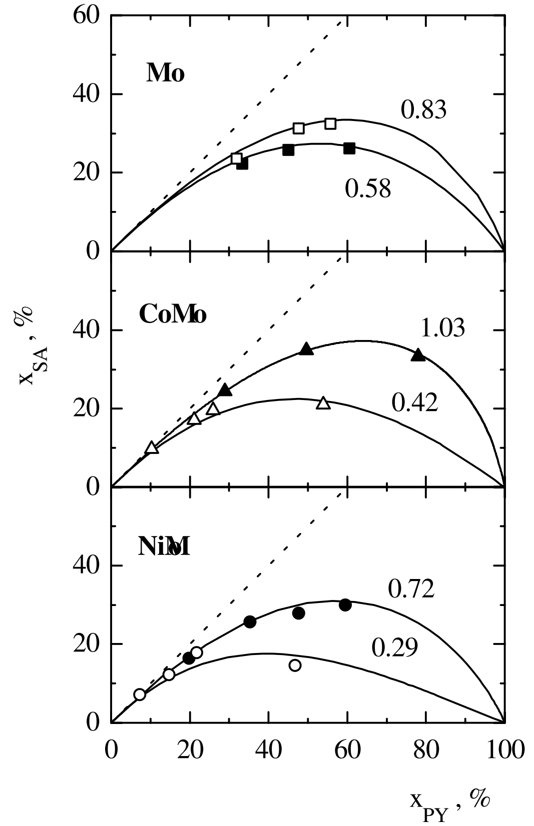

Figure 2. The conversion to saturated amines, SA, during parallel HDN of pyridine and HDS of thiophene. The dashed line is the stoichiometric limitation of x_{SA}. Full and open points are for Al_2O_3- and MgO-supported catalysts respectively. The curves were calculated using the constants k_2 and k_3; the ratio k_2/k_3 is given for each curve.

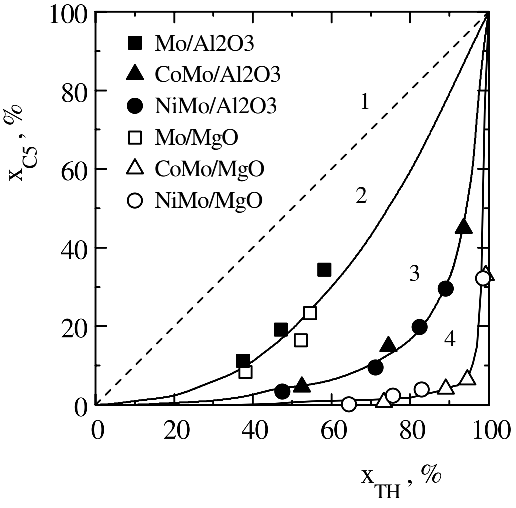

Figure 3. HDN/HDS selectivity in parallel HDN of pyridine and HDS of thiophene. 1 – a hypothetical catalyst of the same HDN and HDS activities; 2 – Mo catalysts; 3 – Co(Ni)Mo/Al_2O_3 catalysts; 4 – Co(Ni)Mo/MgO catalysts.

S_{SA} of MgO-supported Co(Ni) catalysts is distinctly lower than that of their Al_2O_3-supported counterparts. It is concluded that the above-mentioned relation between the magnitude of promotion in HDN and the selectivity to piperidine (or to SA) valid in the field of the above-mentioned three kinetic variables (H_2S/H_2 ratio, H_2 pressure, temperature) does not hold for variable type of support.

The low promotion in HDN activity of Co(Ni)/MgO catalysts leads to their low HDN/HDS selectivity $S_{N/S}$ that is graphically evaluated by plotting HDN conversion versus HDS conversion at the same space time in figure 3. The selectivity $S_{S/N}$ of Mo/MgO and Mo/Al_2O_3 was the same. The promotion of Mo/Al_2O_3 by Co(Ni) results in a decrease in the $S_{S/N}$ because the promotion effect for HDS is higher than that for HDN. However, this decrease for MgO-supported catalysts is even stronger and Co(Ni)/MgO samples exhibit extremely low selectivity to HDN. Remarkably, for the MgO-supported catalysts, the catalytic performance in the competitive HDS/HDN experiment is practically identical for the Ni- and for the Co-promoted MoS_2. For the Al_2O_3-supported MoS_2 catalysts, although the ratio between HDS and HDN is similar, the overall activity differs for promotion using Ni and Co.

It seems generally accepted that not only hydrogenation but also acidic function of the catalyst play an important role in HDN [1,2]. First, adsorption of nitrogen compounds is increased by surface acidity. Second, it is assumed that single C–N bonds formed by hydrogenation of the aromatic pyridine ring are broken by β-elimination catalyzed by acid sites. Which of these steps, hydrogenation or β-elimination, is rate-determining depends on catalyst and reaction conditions. Our unpromoted Mo/MgO and Mo/Al_2O_3 catalysts exhibited the same HDN activity, and it can be speculated that hydrogenation was the rate-determining step and surface acidity was not important over these catalysts. However, promotion with Co and Ni increased hydrogenation activity, β-elimination probably became the rate-determining step and basic Co(Ni)Mo/MgO catalysts were less active than Co(Ni)Mo/Al_2O_3 samples.

A quantitative comparison of the TEM images of sulfidic catalysts supported on various supports is methodically not easy [17]. The problem is also complicated by the important effect of the sulfidation conditions on the emerging MoS_2 structures. After common sulfidation using a H_2S/H_2 mixture at 400 °C, part of MoS_2 is highly dispersed and invisible in *ex situ* obtained TEM images [17,20]. However, some conclusions seem to be well proved. Only the results obtained with commonly sulfided Al_2O_3- or SiO_2-supported samples (H_2S/H_2, 400 °C, 2–3 h) with the content of Mo close to the MoO_3 monolayer in the catalyst precursor are mentioned here. The references given are just examples, other references can be found in the review [17] or recent paper [18]. Basal-bonded MoS_2 slabs strongly predominate over edge-bonded slabs on SiO_2 [18] and Al_2O_3 [17,18]. Most of the slabs seen in Al_2O_3-supported samples consist of 1–3 layers [17,18,21,22] and their mean length is 3–4 nm

[17,21,22] or 1–2 nm [18]. When using quasi *in situ* TEM, however, for specific pretreatment procedures very small (< 1 nm) molybdenum (oxy)sulphide entities are observed [20]. The average slabs' stacking and length is higher on SiO_2 (up to seven layers [18]) than on Al_2O_3. This is attributed to weaker metal–support interaction in SiO_2-supported than in Al_2O_3-supported catalysts [18,23].

While numerous images of Al_2O_3- and SiO_2-supported catalysts are available in the literature, only one previous paper reported TEM images of MgO-supported sulfide catalysts (Mo and NiMo) [13]. However, the catalysts were prepared as mentioned in that paper using aqueous impregnation and calcination at 500 °C for 4 h, and their catalytic activity was low. Furthermore, the TEM images presented in [13] have been recorded *ex situ*, and the MoS_2 slabs are not very clearly visible in the fairly low-magnification images presented. Our Mo/MgO, CoMo/MgO and NiMo/MgO catalysts have been studied using quasi *in situ* TEM/HREM. A representative image is shown in figure 4. This TEM image shows the ordinary slab structure for the sulphided phase. The degree of stacking found for our MgO-supported catalysts does not differ from what is normally found for well-performing Al_2O_3-supported catalysts: many single slabs are present next to some double and triple layers. The slab length distribution is fairly broad. Long slabs are visible when the TEM imaging direction is parallel to the surface of the platelets of MgO. An example is indicated by an arrow labeled "A" in figure 4. These long slabs are oriented parallel to the MgO surface. Short slabs are visible when the TEM imaging direction is perpendicular to the surface of the platelets of MgO. An example is indicated by an arrow labeled "B" in figure 4. These short slabs are oriented perpendicular to the MgO surface.

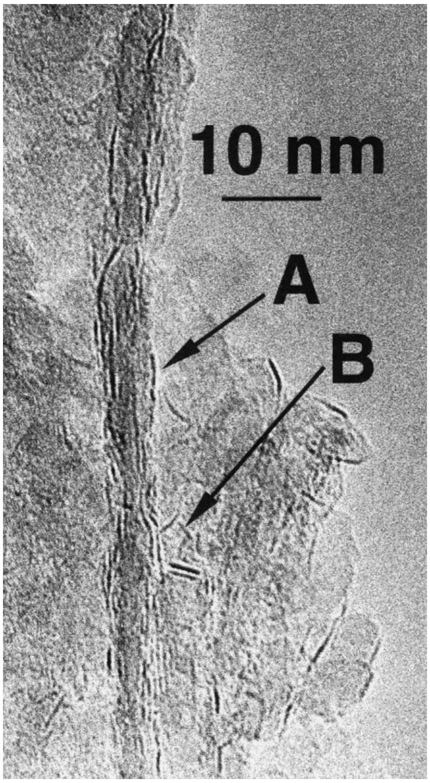

Figure 4. Representative TEM image of sulfided MgO-supported catalysts.

The broad distribution of the MoS_2 crystallites' length has also been reported for Mo/MgO and NiMo/MgO catalysts prepared by aqueous impregnation; crystallites with length up to 8 nm were observed [13]. It was suggested that for the NiMo/MgO catalysts, it was connected with the low surface concentration of Ni caused by the formation of NiO-MgO solid solution during calcination at 500 °C. Ni impedes the lateral growth of MoS_2 slabs by occupying the edge planes. The low Ni surface concentration was indicated by a small promotion effect in HDS activity. However, our results do not support this interpretation. Our catalysts exhibited very high promotion effect (indicating high Ni concentration at MoS_2 edges) but still contained long MoS_2 slabs.

It is now generally accepted in literature that the promotion effect is connected with the decoration of edge planes of MoS_2 slabs with Co or Ni [1]. It follows that the high promotion effect in HDS activity observed in the present work for Co(Ni)/MgO catalysts is probably not connected with the presence of long MoS_2 slabs because the ratio of the surface area of edge to basal planes is low for long slabs. The reason for this high promotion effect remains unclear and requires further study.

4. Conclusions

The Mo/MgO, CoMo/MgO and NiMo/MgO sulfide catalysts were prepared by impregnation using methanol as a solvent instead of water. Starting high surface area MgO (about $250\,m^2\,g^{-1}$) was chemically and texturally stable during such impregnation and the catalysts exhibited higher promotion effect and higher HDS activity in parallel HDS/HDN than their Al_2O_3-supported counterparts. However, their HDN activity only was low. The microstructure of MgO-supported catalysts evaluated by TEM exhibited features mostly similar to conventional Al_2O_3-supported catalysts: characteristic MoS_2 slabs consisting of 1–3 layers were observed. However, the specific features of MgO-supported catalysts as compared to conventional Al_2O_3-supported catalysts were fairly broad slab length distribution and the presence of unusually long MoS_2 slabs.

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