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Nano- and Microscale Engineering of the Molybdenum Disulfide-Based Catalysts for Syngas to Ethanol Conversion

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Nickel-promoted MoS₂, unsupported catalysts and laponitesupported alcohol synthesis catalysts were synthesised by using microemulsion (ME) and hydrothermal (HT) methods. Highly ordered sulfide slabs, consisting of up to seven layers, were visible in the TEM images of HT-based NiMoS₂ catalysts. In contrast, disordered sulfide layers were identified in MEbased NiMoS₂ catalysts. High catalytic activity was observed in ME-based supported (laponite-supported NiMoS₂) and unsupported catalysts. After the CO hydrogenation reaction, the catalysts were characterised by X-ray photoelectron spectroscopy

Introduction

Among the fuel alternatives to gasoline, ethanol has attracted the most research interest.^[1] Ethanol contains oxygen and has a higher octane number than does gasoline. It delivers a sustainable, CO₂ neutral, and clean energy alternative to fuel if sourced from renewable resources. These factors have encouraged the use of ethanol fuel in transport worldwide to reduce the consumption of gasoline. For example, in the United States and Brazil, high-ethanol blends are available as a transportation fuel (e.g., E85, an 85% blend with gasoline).

Currently, ethanol fuel is produced from corn or sugarcane through fermentation; however, there is an increased interest to produce fuel from syngas (a mixture of CO and H_2).^[2] Numerous studies have endeavoured to formulate a cost-effective catalytic process for the production of ethanol from syngas.^[3] Nevertheless, such technology is yet to be implemented because of side reactions, which produce undesired products (methane, methanol, and other hydrocarbons and oxygenates).

Catalysts play a major role in promoting ethanol formation and inhibiting side reactions. Catalysts that are suitable for the conversion of syngas to ethanol can be categorised as rhodi-

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and inductively coupled plasma-mass spectrometry elemental analyses, which detected a significant sulfur loss in ME-based NiMoS₂ catalysts and minor sulfur loss in HT-based NiMoS₂ catalysts. In addition to the large surface area (120 m² g⁻¹), disordered sulfide structure, and exposed active sites, ME-based NiMoS₂ catalysts demonstrated higher alcohol selectivity (61 mol%) than HT-based NiMoS₂ catalysts (15 mol%). Correlations between the catalyst morphology, surface active components, and alcohol selectivity are discussed herein.

um-based catalysts,^[4] modified Fischer–Tropsch synthesis catalysts,^[5] modified methanol synthesis catalysts,^[6] and MoS_2 -based catalysts.^[7]

Herein, we focus on the synthesis and catalytic performance of the MoS₂-based catalyst. Researchers at Dow Chemicals patented the MoS₂-based catalyst in the late 1980s, as a benchscale catalyst testing showed promising results on conversion of syngas to mixed alcohols.^[8] The MoS₂-based catalyst achieved up to 30% CO conversion and 80% ethanol selectivity (CO2 free basis) upon mixing/doping with alkaline metals $(M_{Alk} = K, Cs, Rb)$ and transition metals $(M_{Tr} = Ni, Co, Fe)$.^[9] Most reports state that the alkaline metals promote alcohol formation by preventing reduction of Mo^Ⅳ to Mo^{0[10]} whereas the transition metals increase CO conversion by promoting carbon chain growth.^[11] To obtain the M_{Alk}–M_{Tr}–MoS₂ catalyst, the transition metals are co-precipitated with MoS₂ (ammonium tetrathiomolybdate) precursors^[12] and the alkaline metals are introduced through physical mixing. Most studies aim to find optimum ratios of M_{Alk}/Mo or M_{Tr}/Mo and reaction conditions (pressure, syngas ratio, space velocity, and CO₂ or H₂S addition into feed gas).^[2a, 13] Meanwhile, reports on the synthesis of catalysts and effects of the synthesis parameters on catalyst properties are limited.

The Ni(Co)MoS₂ catalyst, also known as a hydrotreating catalyst, is mainly used to remove sulfur, nitrogen, and oxygen from crude oil feedstock.^[14] According to previous reports, the catalytic activity of MoS₂-based hydrotreating catalysts could be tuned by altering the synthesis parameters.^[15] Devers et al. produced the MoS₂ catalyst through the thermal decomposition and hydrothermal (HT) synthesis of thiosalts; catalytic tests of thiophene hydrodesulphurisation and tetraline hydro-

genation reactions revealed a significant effect of the morphology on the catalytic activity.^[16] By using a solution-based method, Genuit et al. varied synthesis parameters (precursors nature, surfactant types, and $Me_{Ni,Co}/Mo$ ratios) and obtained highly dispersed Ni(Co)–Mo–S sulfides, which led to high catalytic activity in the hydrodesulfurisation of thiophene.^[17]

Furthermore, the catalytic activity of MoS_2 catalysts was affected by the location of promoter atoms (cobalt and nickel) in the sulfide structure.^[18] High catalytic activities were observed in the mixed sulfide ($Me_{Co,Ni}$ –Mo–S) phase, in which the promoter atoms are located on the edge planes of the sulfide layers.^[19] In the mixed sulfide phase, a direct correlation of the catalyst structure with the catalytic performance was confirmed by the Topsøe group.^[20] In non-promoted MoS_2 catalysts, active sites were associated with sulfur vacancies (anionic vacancies), which were formed under a hydrogen-rich environment.^[21] With an atom-resolved scanning tunnelling microscope, Kibsgaard^[22] detected sulfur vacancies by exposing MoS_2 clusters to atomic hydrogen and concluded that the formation of the vacancy (corner or edge) depends on the actual size of MoS_2 nanoclusters.

The catalytic active sites of MoS₂ alcohol synthesis catalysts are expected to be the same as of hydrotreating catalysts.^[23] Most reports lack data indicating a direct correlation between catalytic active sites and catalytic performance (CO conversion and alcohol selectivity) of MoS₂. It is unclear which morphology would best promote the formation of catalytic active sites (sulfur vacancies) and which synthesis route would result in such a morphology/structure. The purpose of this study was to find a correlation between catalytic performance and the morphology/structure of MoS₂. To identify a clear distinction between morphology and structure, we chose the microemulsion (ME) and HT methods for MoS₂ synthesis and compared catalytic activity, alcohol selectivity, and textural properties of both supported and unsupported NiMoS₂ catalysts.

Results and Discussion

Synthesis and characterisation of laponite-supported NiMoS₂ catalysts

The XRD patterns of NiMoS₂-LP-HT, prepared by using the HT method, NiMoS₂-LP-ME, prepared by using the ME method, and the laponite support are shown in Figure 1.

Laponite has a layered structure; the interlayer basal spacing d(001) appeared at $2\theta = 7^{\circ}$ on the XRD patterns. The absence of the basal peak ($2\theta = 7^{\circ}$) indicated either 1) complete exfoliation of laponite layers or 2) chemical decomposition of laponite via acid leaching during synthesis.^[24] Laponite retained its layered structure during syntheses (HT and ME), as XRD detected the basal ($2\theta = 7^{\circ}$) peak in all three samples. The XRD pattern of NiMoS₂-LP-HT mainly consisted of laponite and MoS₂ phases (Figure 1). NiMoS₂-LP-ME generated weak XRD signals, which indicated the amorphous nature of samples (Figure 1). The TEM images of the samples are shown in Figure 2. An image of commercial bare laponite is also provided to clarify laponite structures.



Figure 1. XRD patterns of NiMoS₂-LP-HT, NiMoS₂-LP-ME, and bare laponite.



Figure 2. TEM images of a) NiMoS₂-LP-HT, b) NiMoS₂-LP-ME, and c) bare laponite. Scale bars = 200 (a, b) and 50 nm (c).

The TEM images of NiMoS₂-LP-HT and NiMoS₂-LP-ME revealed dark catalyst particles distributed on the laponite support. The TEM image of NiMoS₂-LP-HT consisted of large aggregates (≈ 200 nm), which were irregularly distributed across the laponite framework. In contrast, the TEM image of NiMoS₂-LP-ME resembled the ideal morphology of a catalyst, in which fine particles (≈ 20 nm) of active species were homogenously deposited on the support. A comparison of the TEM images of NiMoS₂-LP-HT and NiMoS₂-LP-ME catalysts revealed that the ME method results in an ideal catalyst structure, which has uniformly distributed NiMoS₂ particles on the laponite framework.

The nitrogen physisorption isotherms of the two catalysts corresponded to type IV isotherms, which are characteristic of mesoporous adsorbents (Figure 3).^[25] The BET surface area of



Figure 3. Nitrogen physisorption isotherms and PSD curves of NiMoS_2-LP-HT and NiMoS_2-LP-ME catalysts. w = Pore width

300 and 250 m^2g^{-1} was measured for the NiMoS₂-LP-ME and NiMoS₂-LP-HT catalysts, respectively. The pore size distribution (PSD) curves of the two catalysts are compared in the inset of Figure 3.

A bimodal PSD was observed for catalysts, which was centred at 3.5 and 5.1 nm for NiMoS₂-LP-HT and at 3.5 and 7.1 nm for NiMoS₂-LP-ME. Regardless of the different synthesis methods used, both catalysts demonstrated an average pore size of 3.5 nm (the BJH method). This pore size could arise from spaces between randomly oriented MoS₂ layers. Compared with the HT-based sample, the ME-based sample had a broader PSD. The broad PSD was possibly due to the non-ionic surfactant (Brij 30) used as an ME stabiliser; the surfactant decomposed during heat treatment, which left a porous structure and amorphous carbon residue.

Catalytic performances of laponite-based NiMoS₂ catalysts

The catalytic performances of laponite-supported NiMoS₂ catalysts were studied at the laboratory scale in a fixed-bed highpressure reactor. By using the measured volumetric flow rate and the concentration of component *i*, the molar flow rate of component *i* was determined (F_i). The CO conversion was calculated by using the molar flow rates of CO in the inlet and outlet stream of the reactor. The internal standard gas (nitrogen) was used to calculate molar flow rates of CO in the outlet stream [Eq. (1)].

$$X_{\rm CO} = \frac{F_{\rm CO}^{\rm in} - F_{\rm CO}^{\rm out}}{F_{\rm CO}^{\rm in}} \tag{1}$$

The selectivity of a product was calculated by using Equation (2). Notably, CO_2 content is included in the calculation of selectivity.

$$S_{\text{ethanol}} = \frac{F_{\text{ethanol}}^{\text{out}}}{F_{\text{CO}}^{\text{in}} - F_{\text{CO}}^{\text{out}}}$$
(2)

To study CO conversion and the stability of the laponite-supported $NiMoS_2$ catalyst, the CO hydrogenation reaction was performed at T=310 °C, P=60 bar (1 bar = 100 kPa), and gas hourly space velocity (GHSV) = 1044 h⁻¹.

The catalytic test results of the two catalysts are presented in Figure 4 and Table 1. The NiMoS₂-LP-HT catalyst maintained stable CO conversion during the 95 hour reaction run; the NiMoS₂-LP-ME catalyst had high initial activity, which quickly decreased with reaction time. The average CO conversion reached up to 14.5 mol% with NiMoS₂-LP-ME, whereas only 9.45 mol% of CO was converted into products with NiMoS₂-LP-HT.



Figure 4. CO conversion as a function of time on stream for NiMoS₂-LP-HT and NiMoS₂-LP-ME catalysts performed at 310 $^{\circ}$ C, 60 bar, and a GHSV of 1044 h⁻¹.

Variable	NIMOS -I P-HT	NiMoS -I P-ME				
Vallable						
X _{co} ^[b] [mol %]	9.45	14.5				
S ^(c) [mol%]						
hydrocarbons	51.4	34.2				
C ₁ -OH	3.9	19.1				
C ₂ –OH	26.4	18.2				
C ₃ –OH	2.6	3.39				
other oxygenates	0.3	1.71				
alcohol	33.2	42.4				
C_2 -OH in total alcohol [mol %]	79.5	43.2				
[a] Reaction conditions: $P=60$ k conversion: [c] Selectivity based	par, GHSV = 1044 h ⁻¹	, $H_2/CO = 2$				

Although NiMoS₂-LP-ME resulted in high CO conversion (14.5 mol%), methane and methanol were the major outstream products with 34 and 19 mol% selectivity, respectively.

To clarify the differences in the catalytic performance of the two catalysts, X-ray photoelectron spectroscopy (XPS) analysis was performed (Figure 5). The aim was to quantify surface elements and compare the quantity of surface elements in $NiMoS_2$ -LP-HT and $NiMoS_2$ -LP-ME catalysts. Notably, the XPS results were obtained from a survey (general) scan without further details on the oxidation state of the elements. As samples



Figure 5. XPS results of NiMoS₂-LP-HT and NiMoS₂-LP-ME. High-resolution scan in Mo3d, S2p, and Ni2p regions. $CPS = Counts s^{-1}$.

were exposed to air during preparation for XPS, the catalysts were not reduced before XPS analysis. Carbon and oxygen were the major elements on the surface of both catalysts (Table 2). The atomic percentage of elements in NiMoS₂-LP-HT changed as follows: 1) the molybdenum content remained unchanged, 2) the sulfur content reduced from 5.48 to 4.37 at%, and 3) the nickel content equalled 1.31 at% before and 0.82 at% after the reaction on the surface.

The XPS results of the ME-based samples, in which the surface concentration of active species (molybdenum, nickel, and sulfur) was three times lower than that in the HT-based samples (in fresh catalysts), are also summarised in Table 2. Sulfur was not detected in the spent NiMoS₂-LP-ME catalysts, whereas the surface concentration of nickel and molybdenum decreased after the reaction.

Table 2. XPS data of $NiMoS_2\text{-}LP$ prepared by using HT and ME methods, analysed before and after reaction tests.^{(a)}						
Element	NiMoS ₂ -LP-ME ^F	XPS dat NiMoS ₂ -LP-ME ^S	a [at %] NiMoS ₂ -LP-HT ^F	NiMoS ₂ -LP-HT ^s		
Mo 3d	1.91	1.7	2.74	2.8		
Ni2p	0.2	0.14	1.31	0.82		
S2p	1.05	0	5.48	4.37		
Mg 2s	5.7	8.0	6.67	7.3		
Si 2p	15.6	18.0	12.09	12.7		
C1s	37.3	32.68	25.12	23.1		
O1s	38.23	39.02	46.59	48.79		
[a] F=fresh catalysts; S=spent catalysts.						

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In the XPS of NiMoS₂-LP-ME catalysts, laponite species (magnesium, silicon, and oxygen) dominated on the surface, which could act as a barrier between catalyst species (molybdenum, nickel, and sulfur) and reactant molecules (carbon monoxide and hydrogen). In the ME method, NiMoS₂ particles were formed in a reverse emulsion (water-in-oil) system and their particle sizes were less than 5 nm (some of them formed aggregates up to \approx 20 nm); laponite particles $(d_{\rm p} \approx 30 \text{ nm})$ were dispersed in water without further size reduction. The different particle size likely caused the presence of most laponite particles on the surface layers of the catalyst; thus, laponite particles generated stronger XPS signals than did NiMoS₂ particles. This observation could explain why laponitesupported (NiMoS₂-LP-ME) catalysts failed to deliver high catalytic activity.

The above results were based on the textural and catalytic properties of laponite-supported NiMoS₂ catalysts prepared by using HT and ME methods. The ME method produced NiMoS₂-LP with more superior catalytic performances than the HT-based catalysts. A comparison of TEM images revealed that the ME method resulted in homogenously distributed NiMoS₂ particles on the laponite support. According to the XPS results, the surface of NiMoS₂-LP-ME was covered by laponite species (magnesium, silicon, and

oxygen); however, a greater exposure to the active sites (molybdenum, nickel, and sulfur) was needed to achieve high CO conversion. For further comparisons, a new set of unsupported NiMoS₂ catalysts was prepared by using the ME and HT methods.

Catalytic performances of unsupported NiMoS₂ catalysts

Unsupported NiMoS₂-HT and NiMoS₂-ME catalysts were also tested for the CO hydrogenation reaction at T = 310 °C and P = 60 bar. Changes in CO conversion with time on stream are illustrated in Figure 6. In the catalytic tests with NiMoS₂-HT, the CO conversion level remained stable during 92 h of reaction whereas the activity of NiMoS₂-ME decreased in the last 10 h of reaction. High catalytic activity was observed for NiMoS₂-ME



Figure 6. CO conversion as a function of time on stream for NiMoS₂-HT and NiMoS₂-ME catalysts performed at 310 °C, 60 bar, and a GHSV of 1044 h^{-1} .

catalysts, which resulted in an average CO conversion of 33 mol %. In contrast, NiMoS₂-HT catalysts converted only 23 mol % of CO into products.

The product selectivity of the catalysts is given in Table 3. With the NiMoS₂-HT catalyst, CO hydrogenation mainly yielded methane (30.2 mol%) and carbon dioxide (43.8 mol%), which

Table 3. CO conversion and selec catalysts. ^[a]	tivity of NiMoS ₂ -H	IT and NiMoS ₂ -ME
Variable	NiMoS ₂ -HT	NiMoS ₂ -ME
X _{co} ^[b] [mol%]	23	33
S ^[c] [mol %]		
hydrocarbons	30.2	14.4
C1-OH	5.25	28.1
C ₂ –OH	8.7	26.8
C ₃ OH	0.75	4.27
other oxygenates	0.28	1.83
alcohol	15	61
C ₂ -OH in total alcohol [mol %]	58	44
[a] Reaction conditions: $P = 60$ bar	$GHSV - 1044 h^{-1}$	$H/CO = 2 \cdot [b] CO$

[a] Reaction conditions: P = 60 bar, GHSV = 1044 h⁻¹, H₂/CO = 2; [b] CO conversion; [c] Selectivity based on C-containing products, including CO₂.

indicated a low selectivity for the formation of alcohol. The ME -based catalysts resulted in a high percentage of alcohol (61 mol%) and significantly a low amount of methane (14.4 mol%) and carbon dioxide (23 mol%). As the same amount of the NiMoS₂ active catalyst was loaded into the reactor for both cases, such a significant difference in catalytic properties was unexpected, particularly in product selectivity.

To clarify the major differences between the unsupported HT- and ME -based catalysts, TEM and SEM analyses were performed. As shown in TEM (Figures 7) and SEM (Figure 8) images, the morphology of NiMoS₂ depended on the synthesis method. The TEM images of the NiMoS₂-ME catalyst demonstrated highly disordered MoS₂ layers; in some areas, up to three layers were detected. In contrast, stacks of MoS₂ containing six to seven sulfide layers and well-crystallised sulfide slabs were observed on the TEM images of the NiMoS₂-HT catalyst. These TEM images indicated that the ME method produced highly disordered and short sulfide layers (\approx 10 nm) whereas the HT method produced continuous and well-crystallised multilayers of MoS₂. The SEM images indicated that the NiMoS₂-ME catalyst contained small and plate-shaped particles whereas the NiMoS₂-HT catalyst consisted of large aggregates.



Figure 7. TEM images of unsupported a) NiMoS₂-HT and b) NiMoS₂-ME catalysts. Scale bars = 20 nm (a) and 10 nm (b).



Figure 8. SEM images of a) unsupported NiMoS2-HT and b) NiMoS2-ME catalysts. Scale bars = 10 $\mu m.$

By using nitrogen physisorption isotherms, we measured a BET surface area of $120 \text{ m}^2 \text{g}^{-1}$ and a pore volume of 0.45 mL for NiMoS₂-ME catalysts. A BET surface area of $6 \text{ m}^2 \text{g}^{-1}$ was found for NiMoS₂-HT catalysts. The TEM and SEM images of the HT-based catalysts showed highly ordered sulfide slabs, which was in agreement with the small BET surface area and pore volume found for the sample. A large BET surface area of the NiMoS₂-ME catalyst was associated with the highly disordered sulfide layers and carbon residue (26 wt %); the latter may act as a dispersant for particles by creating a porous network.

Surface analysis of unsupported NiMoS₂ catalysts

The major differences were found in the XPS data of the HTand ME-based catalysts; an XPS analysis was performed for the fresh and spent catalysts. The XPS spectra and one example of curve fittings are presented in Figure 9a and b (see the Supporting Information for detailed curve fitting). An XPS survey scan of the fresh NiMoS₂-ME catalyst demonstrated strong signals of oxygen and carbon, O1s and C1s, and weak signals of Mo3d and S2p (Table 4). The NiMoS₂-ME catalyst yielded a binding energy of 229.3 and 232.7 eV, which were characteristic of Mo 3d_{5/2} (Mo⁴⁺) and Mo 3d_{5/2} (Mo⁶⁺), respectively.^[15b] An analysis of the XPS spectrum of the sulfur region revealed two $S2p_{3/2}$ doublets with a binding energy of 162 and 164 eV, which indicated the presence of S^{2-} ions and S_2^{2-} groups.^[26] Correlating the XPS spectra of sulfur (S2p), molybdenum (Mo3d), and a S/Mo atomic ratio of 2, we assigned a binding energy of 229.3 eV to MoS₂; however, this does not exclude the presence of MoO₂.

The analysis of the XPS spectra revealed a small peak at 229.3 eV, which was characteristic of Mo $3d_{5/2}$ (Mo⁴⁺), in Mo 3d regions of the spent NiMoS₂-ME catalyst. In addition, the spectrum demonstrated some contribution from Mo⁵⁺ with 230.9 eV and a large peak corresponding to Mo $3d_{5/2}$ (Mo⁶⁺) with a binding energy of 232.8 eV. Measurements in the S 2p region detected sulfur in a significantly low concentration (2.3 at%), which yielded one S $2p_{3/2}$ doublet with a binding energy of 162.2 eV. The surface atomic ratio of S/Mo corresponded to 0.33. An increase in Mo $3d_{5/2}$ (Mo⁶⁺) contribution and low sulfur content indicated that a significant amount of sulfur was lost during the reaction, which led to the oxidation of Mo⁴⁺ species to Mo^V and Mo^{VI} oxides.

The XPS spectra of $NiMoS_2$ -HT catalysts are shown in Figure 9a and b. A minor difference was observed in XPS data of

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Figure 9. a) XPS results of fresh and spent NiMoS₂-HT and NiMoS₂-ME catalysts. High-resolution scan in Mo3d regions. b) XPS results of fresh and spent NiMoS₂-HT and NiMoS₂-ME catalysts. High-resolution scan in S2p regions.

	$NiMoS_2-ME^F$	NiMoS ₂ -ME ^s	$NiMoS_2$ -HT ^F	NiMoS ₂ -HT ^s	
XPS data [at %]					
Mo 3d	5.16	6.89	7.98	8.59	
S 2p	10.16	2.31	15.13	17.16	
Ni 2p	0	1.19	1.76	1.82	
C 1s	67.14	61.9	39.45	33.54	
O1s	17.56	27.72	35.03	38.89	
Surface composition ^[b]	Ni ₀ MoS _{1.96}	Ni _{0.17} MoS _{0.33}	Ni _{0.22} MoS _{1.89}	Ni _{0.21} MoS _{1.99}	
Elemental composition ^[c]	Ni _{0.41} MoS _{1.93}	Ni _{0.48} MoS _{0.75}	Ni _{0.43} MoS _{2.11}	Ni _{0.47} MoS _{1.77}	

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the fresh and spent $NiMoS_2$ -HT catalysts, particularly in the concentration of surface elements and in Mo3d and S2p line positions (Table 4).

The fresh NiMoS₂-HT catalysts in Mo3d regions contained three molybdenum oxidation states: 1) Mo3d_{5/2} (Mo⁴⁺) at 229.3 eV; 2) Mo3d_{5/2} (Mo⁵⁺) at 230.6 eV; 3) Mo3d_{5/2} (Mo⁶⁺) at 232.8 eV; these line positions remained unchanged in the spent NiMoS₂-HT catalysts. Regarding the S2p regions, a weak and broad shoulder at 169 eV, which is consistent with S2p_{3/2} for SO₄ groups, existed together with two S2p_{3/2} doublets at 162.2 and 164.5 eV, respectively. Compared with the NiMoS₂-ME catalyst, the NiMoS₂-HT catalyst retained its surface sulfur content during catalytic testing, which gave a S/Mo atomic ratio of 2 for both fresh and spent NiMoS₂-HT catalysts.

The total concentration of (molybdenum, nickel, and sulfur) elements in fresh and spent catalysts was also analysed by using inductively coupled plasma-mass spectrometry (ICP-MS), and the results are summarised in Table 4. The ICP-MS results revealed that the NiMoS₂-ME catalyst lost a significant amount of sulfur during the reaction, which concurs with the XPS results. The chemical composition of the NiMoS₂-ME catalyst changed from Ni_{0.41}MoS_{1.93} to Ni_{0.48}MoS_{0.75} after the reaction; in the NiMoS₂-HT catalyst, the composition changed to Ni_{0.43}MoS_{2.11} (fresh) and Ni_{0.47}MoS_{1.77} (spent).

Correlation between sulfur loss and catalytic activity

During the exposure of the MoS_2 catalyst to the syngas feed, a loss of sulfur was observed. According to previous reports, sulfur located on the edges of the sulfide layers reacts with hydrogen, which leaves coordinatively unsaturated molybdenum ions and anionic vacancies.^[21,27] In hydrotreating MoS_2 catalysts, the adsorption of molecules such as O_2 , CO, N_2 , and NH_3 occurred mainly on the anionic vacancy sites of sulfide catalysts.^[28] A correlation between the active sites and the improved catalytic activity was reported for hydrotreating catalysts.^[29] For other sulfide catalysts (NiWS) used in hydrocracking, hydrodesulfurisation, and hydrogenation reactions, the anionic vacancies (sulfur-deficient metal sites) were the catalytic active centres; these could be blocked in the presence of $H_2S.^{[30]}$ A similar phenomenon could also occur with the MoS_2 catalyst during the alcohol synthesis reaction. The catalyst, pre-

> pared by using ME methods, had higher selectivity towards alcohol than towards hydrocarbons. Based on the XPS results, which revealed a substantial decrease in sulfur content after the reaction [Ni₀MoS_{1.96} (fresh); Ni_{0.17}MoS_{0.33} (spent)] and catalytic tests, it is possible to correlate the high alcohol selectivity with the coordinatively unsaturated molybdenum sites. Assuming that any alcohol precursors originate from the coordinatively unsaturated molybdenum sites, a possible mechanism for alcohol formation could be drawn as shown in Scheme 1.

This mechanism supports the reaction path in which non-dissociated CO molecules are absorbed into CH_3 -metyl species, which is also reported by Mei and other researchers.^[31] As the NiMoS₂-ME catalysts



Scheme 1. Mechanism for the formation of ethanol via adsorption of CO molecules in sulfur-vacancy molybdenum sites.

contain layered sulfide (up to two layers), sulfur located on other than surface planes and edge sites most likely remains in the structure and contributes to the formation of CH_3 -metyl species through the CO and H_2 dissociation occurring on charge neutral molybdenum sites or fully sulfurised molybdenum sites. Moreover, the dissociation of hydrogen on sulfurdeficient sites could not be ruled out.

A further question arises as to whether these coordinatively unsaturated molybdenum sites are stable. Product selectivity and CO conversion change over time; other factors (in addition to sulfur loss) also lead to the change in catalytic activity, such as pore blocking, particle sintering, and carbon deposition. Hensley et al. claimed that the presence of a sulfur source (H_2S) in the syngas feed is crucial because the Mo^{IV} catalyst oxidises over time to form Mo^{VI} oxides, which changes selectivity from alcohol to hydrocarbons.[32] However, in their study, the presence of H₂S in the syngas feed resulted in 81% alcohol and 17% hydrocarbon selectivity (D6-sample name, please see Ref. [32]) whereas the catalyst (D2) tested in H_2S -free syngas yielded 77 % alcohol and 19% hydrocarbon selectivity. The differences in product selectivity are not apparent, considering these reactions have continued for 350 (D2) and 3840 h (D6), respectively. The study by Christensen et al.[13a] also observed differences in product selectivity. Upon addition of H_2S , they found chain growth and increase in selectivity towards hydrocarbons. It is most likely that H₂S reacts with reaction intermediates and promotes the formation of long chains of hydrocarbons. By using H_2S -free syngas feed, Gang et al.^[13b] observed no apparent change in the catalytic activity and alcohol selectivity of the K-Mo/Co/C sulfide catalyst after 1000 h of reaction. Dianis^[33] observed a decrease in the alcohol selectivity of MoS₂ with feed containing 150 ppm H₂S; in contrast, the alcohol selectivity of a Co-Mo-S catalyst was unaffected by H₂S addition. They postulated that the increased alcohol selectivity is the result of the weakly adsorbed hydrogen and strongly adsorbed CO. As numerous reactions occur simultaneously on the surface of a catalyst, the possibility of blocking the coordinatively unsaturated molybdenum sites is high; however, their presence plays a major role in alcohol synthesis. If there is a sudden decrease in alcohol selectivity, one must perform a treatment of the catalyst with the sulfur source (H₂S). Cofeeding with a sulfur source (H₂S) during the reaction inhibits the formation of coordinatively unsaturated molybdenum sites and changes the product selectivity of a catalyst. On the basis of data presented herein, we conclude that the ME method produces highly active NiMoS₂ catalysts with higher ethanol selectivity than the HT method. The ME-based catalyst has disordered sulfide structures, sulfur vacancies, and large BET surface area. Our results emphasise that the highly disordered sulfide structures in combination with coordinatively unsaturated molybdenum sites is the basis for the synthesis of ethanol from syngas.

Conclusions

The aim of this study was to synthesise highly active catalysts for ethanol synthesis from syngas. A number of NiMoS₂ catalysts (laponite supported and unsupported) were synthesised by using the hydrothermal and microemulsion (ME) methods. The unsupported NiMoS₂ catalyst prepared by the using ME method demonstrated a larger BET surface area (120 m^2g^{-1}), higher CO hydrogenation activity (33 mol% CO conversion), and higher selectivity toward alcohol (61 mol%) than those prepared by using the hydrothermal-based NiMoS₂ catalyst. The X-ray photoelectron spectroscopy and inductively coupled plasma-mass spectrometry results of the spent catalysts revealed a significant loss of sulfur, particularly in NiMoS₂-ME catalyst. The high catalytic activity of the NiMoS₂-ME catalyst is associated with its highly disordered sulfide layers, which are readily reduced in syngas atmosphere by releasing sulfur from its structure. The release of sulfur from the catalyst structures creates anionic vacancies that promote the formation of alcohol via CH₃-methyl and CO coupling.

Experimental Section

Laponite-supported NiMoS₂-ME catalyst preparation

The clay, Laponite RD (Laporte Industries Ltd, USA), was used as a support material. The laponite powder (0.5 g) was dispersed in water (50 mL). The suspension was stirred until it formed an opaque solution. Meanwhile, the oil phase containing cyclohexane (100 mL) and a non-ionic surfactant (6 mL; Brij-30, Sigma-Aldrich) was stirred in a beaker at RT. Then, a sulfur source (5 mL; 21 wt% (NH₄)₂S solution, Sigma–Aldrich) was added to the oil phase. After several minutes of stirring, an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (2 mL, 25 wt%; Sigma–Aldrich; 83.0% MoO₃ basis) was added dropwise to the water-in-oil (w/o) ME, which was followed by the addition of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1 mL; 37.5 wt%; Sigma-Aldrich). The black w/o ME system was stirred for 1 h to allow sufficient mixing. Laponite (dispersed in 50 mL of water) was added to the w/o ME system. The addition of laponite destabilised w/o ME systems, which led to the deposition of precipitants (molybdenum, nickel, and sulfur) onto the laponite surface. Subsequently, cyclohexane was removed with a rotary evaporator. The black precipitate was heat-treated in N₂ atmosphere at 350 °C for 4 h to remove the surfactant.

Unsupported NiMoS₂-ME catalyst preparation

The experimental method was the same as that for the supported catalysts, except the laponite solution (laponite/water) was not added.

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Laponite-supported NiMoS₂-HT catalyst preparation

The laponite-supported NiMoS₂ catalyst was prepared by using the HT method as follows: Laponite (5 g) was dispersed in water (250 mL). The suspension was stirred until it formed an opaque solution. The surfactant (10 mL; TERGITOL 15-S-9, Sigma–Aldrich) was added to the laponite solution. The suspension was then stirred for 2 h to allow sufficient mixing. Meanwhile, two aqueous solutions of $(NH_4)_2MoS_4$ and $Ni(NO_3)_2$ were prepared. These two solutions were added dropwise over a 1 h period to the stirred suspension (laponite/surfactant/H₂O). The Mo/Ni molar ratio was 2:1. After prolonged stirring for 3 h at 60 °C, the resulting black slurry was transferred to an autoclave and kept at 130 °C for 24 h. The black precipitate was recovered from the mixture by centrifuging and washing with deionised water. The wet cake was dried in air at 100 °C, followed by heat-treatment at 350 °C for 4 h in N₂ atmosphere.

Unsupported NiMoS₂-HT catalyst preparation

The experimental method was the same as that for the supported catalysts, excluding the addition of the laponite solution (laponite/ H_2O).

Catalyst characterisation

The crystalline phase of the laponite-supported NiMoS₂ catalyst was identified with X-ray diffractometer (MiniFlex) using CoK_a radiation. The internal morphology of the samples was observed with a high-resolution transmission electron microscope (JEOL-2100) operating at 200 kV. The N₂ adsorption/desorption isotherms of the samples at -196 °C were obtained with a TriStar II surface analyser (Micromeritics). The XPS data were obtained with an Axis Ultra Xray photoelectron spectrometer (Kratos) equipped with a 165 mm hemispherical electron energy analyser. The incident radiation was monochromatic AlK_{α} X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Survey (wide) scans were taken at an analyser pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV. Survey scans were taken in the binding energy range of 1200-0 eV with 1.0 eV steps and 100 ms dwell time. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} Torr (1 Torr = 133.3 Pa), and during sample analysis, it was 1.0×10^{-8} Torr. Atomic concentrations were calculated with the CasaXPS software (version 2.3.14) and a Shirley baseline with Kratos library relative sensitivity factors. The peak fitting of the high-resolution data was also performed with the CasaXPS software. A CHNS elemental analyser (FlashEA 1112 series, Thermo Electron Corporation) was used to determine the carbon content.

The catalytic tests were performed at 310 °C, 60 bar, and a GHSV of 1044 h^{-1} in a fixed-bed high-pressure reactor. The stainless steel fixed-bed reactor (internal diameter: 10 mm; length: 100 mm) equipped with a thermocouple was inserted in a furnace. The catalyst was reduced in H₂ atmosphere at 450 °C for 4 h before the reaction. In all catalytic tests, premixed syngas with a H₂/CO ratio of 2:1 and 4% of N₂ (internal standard) was used as a feed. The mass flow controller (Bronkhorst High-Tech B.V.) regulated the inlet gas flow rate. Gaseous products leaving the reactor was passed through the condenser to obtain the liquid fraction of products. The outlet gas stream composition was analysed with a gas chromatograph (GC-2014, Shimadzu) equipped with a thermal conductivity detector. Liquid samples were discharged from the condenser

every 12 h and analysed with a gas chromatograph (GC-8A, Shimadzu) equipped with a flame ionisation detector.

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