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Communication

Sulfided Mo/Al₂O₃ hydrodesulfurization catalyst prepared by ethanol-assisted chemical deposition method

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ABSTRACT

In this communication, we report a novel strategy to prepare a MoS₂/Al₂O₃ hydrodesulfurization (HDS) catalyst by thermally treating a MoS₃/Al₂O₃ precursor in H₂ atmosphere. In our approach, the active phase precursor MoS₃ was first prepared using thioacetamide and sodium molybdate as sources of S and Mo, respectively, and ethanol as a dispersant. The precursor was deposited onto the surface of a γ-Al₂O₃ support and heat-treated to form the catalyst. The catalyst was characterized by N₂ adsorption-desorption, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy. The HDS activity of the catalyst was assessed using dibenzothiophene as a model reactant. The catalyst possessed larger specific surface area and pore volume, higher dispersion and degree of sulfidation of Mo species, and shorter and more suitable stacking of MoS₂ slabs, resulting in superior catalytic activity compared with a catalyst with the same metal content prepared by the conventional impregnation method. Ethanol could disperse the precursor MoS₃ particles via “S...H-O” H-bonding to lessen their aggregation.

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Hydrodesulfurization (HDS) is an important process in the modern petroleum refining industry that is used to produce clean transportation fuels. Developing HDS catalysts with improved activity is the most cost-effective approach to increase the efficiency of HDS [1]. Mo/Al₂O₃ catalysts containing MoS₂ as the active phase have been the main commercial HDS catalyst system for more than half a century [1,2]. It is generally accepted that there are two types of MoS₂ active phases: type I and type II [2–5]. The type I phase usually consists of stacked monolayers and thus is well dispersed. However, it interacts strongly with the support alumina via Mo–O–Al linkages, which leads to poor sulfidation of Mo species and thereby lowers the activity of the MoS₂ active phase. In contrast, the type II phase

is highly stacked and interacts weakly with the support alumina, resulting in full sulfidation of Mo species and thereby higher activity of the MoS₂ active phase. For this reason, increasing the dispersion of active metal sulfides to obtain sufficient active sites while weakening the metal-support interaction to promote the sulfidation of Mo species has been the main focus in preparing high-efficiency HDS catalysts [6].

The commercial preparation of Mo-based HDS/hydrotreating catalysts is usually realized by impregnating γ-Al₂O₃ extrudates with an aqueous solution of ammonium heptamolybdate, followed by aging, drying and calcining to produce oxidic MoO_x/Al₂O₃ catalysts that are sulfided prior to use with sulfidation agents such as a mixture of H₂S and H₂ [2]. Many studies

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have shown that in the conventional impregnation process [7–9], the heptamolybdate anions interact strongly with the surface of alumina, giving rise not only to an eggshell-like uneven distribution of the Mo species, but also strong Al–O–Mo linkages after calcination, which leads to incomplete sulfidation and thereby the formation of type I phase with low activity. Importantly, during impregnation of the support, readily solubilized aluminum species present in alumina can react with heptamolybdate anions to form Anderson-type heteropolyanions, e.g., $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$, which are transformed into bulk MoO_3 crystals and $\text{Al}_2(\text{MoO}_4)_3$ species during calcination [10,11]. These two species are difficult to fully sulfide, and therefore detrimental to the performance of the resulting catalysts [10]. The combination of well-dispersed metal species with a high degree of sulfidation cannot be achieved using the conventional preparation method. In addition, the on-site sulfidation of HDS catalysts in the form of oxides using sulfidation agents such as methyl disulfide also possesses some problems, such as long start-up time, serious equipment corrosion, and potential hurt to human body [12]. For this reason, there has been a growing tendency to use presulfided HDS/hydrotreating catalysts in the refining industry in recent years. In general, the procedure used to prepare presulfided catalysts involves two steps: the deposition of sulfided precursors, such as soluble thiomolybdate or thiotungstate salts, into the pores of the support, and high-temperature thermal treatment of the supported sulfided precursors to obtain the active phases [13–15]. These methods are still being developed, and require further investigation.

Herein we report a novel strategy to directly prepare a sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ HDS catalyst using MoS_3 nanoparticles as the precursor of the active phase. In our approach, MoS_3 particles are first synthesized by homogeneous precipitation between thioacetamide (CH_3CSNH_2 , TAA) and MoO_4^{2-} anions in the presence of H^+ at about 84 °C, to which a given amount of ethanol is added to control the size of the MoS_3 particles. These MoS_3 nanoparticles are then deposited onto the surface of alumina to obtain the precursor $\text{MoS}_3/\text{Al}_2\text{O}_3$ composite. Finally, a sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst with high dispersion and sulfidation degree of Mo species is successfully obtained by reduction of the $\text{MoS}_3/\text{Al}_2\text{O}_3$ composite at high temperature in the presence of H_2 . For comparison, another sulfided $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst with identical Mo content was prepared by the conventional impregnation method. The two catalysts are characterized by N_2 adsorption-desorption, X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM), and their HDS performance is evaluated using dibenzothiophene (DBT) as a model reactant.

Except for $\gamma\text{-Al}_2\text{O}_3$ pellets (20–40 mesh, surface area 215 m^2/g , pore volume 0.51 ml/g , Shandong Aluminum Plant, the People's Republic of China), all of the chemicals used in this work were of analytical grade.

Typical ethanol-assisted chemical deposition was carried out as follows. First, aqueous HCl (4.5 ml, 0.24 mol/L) was added into a stirred aqueous solution (30 ml) of sodium molybdate (Na_2MoO_4 , 0.006 mol/L) and TAA (0.019 mol/L). Anhydrous ethanol (30 ml) was added dropwise to the stirred

solution and the resulting solution was transferred to a 100-ml rotary Teflon-lined stainless steel autoclave containing $\gamma\text{-Al}_2\text{O}_3$ extrudates (3.0 g) and heated at 84 °C for 24 h. The resulting $\text{MoS}_3/\text{Al}_2\text{O}_3$ composite (denoted EA- $\text{MoS}_3/\text{Al}_2\text{O}_3$) was filtered, washed with deionized water and anhydrous ethanol, respectively, and then dried at 50 °C in N_2 atmosphere for 6 h. EA- $\text{MoS}_3/\text{Al}_2\text{O}_3$ was then treated in H_2 flow at 500 °C for 4 h, yielding the $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst (denoted EA-Sul-CAT). The MoO_3 loading in EA-Sul-CAT determined by X-ray fluorescence spectroscopy (XRF, Rigaku ZSX-100e) was 16 wt%. For comparison, a conventional catalyst with the same MoO_3 content was prepared by incipient wetness impregnation of $\gamma\text{-Al}_2\text{O}_3$ extrudates with an aqueous solution of ammonium molybdate. The impregnated extrudates were dried at 120 °C for 2 h and then calcined at 500 °C for 4 h in air to yield an oxidic $\text{MoO}_3/\text{Al}_2\text{O}_3$ composite, which was sulfided with a mixture of 3 wt% CS_2 in cyclohexane at a temperature of 300 °C, liquid hourly space velocity (LHSV) of 8 h^{-1} , total pressure of 4.0 MPa, and H_2 /hydrocarbon volumetric ratio of 400 to obtain the sulfided catalyst (denoted IM-CAT). In addition, to determine the role of ethanol in the preparation process, another sulfided catalyst, EF-Sul-CAT, with the identical MoO_3 content was also prepared by the same procedure as used for preparing EA-Sul-CAT, except that water was used instead of anhydrous ethanol in the second step.

Precursors and catalysts were characterized by HRTEM (Philips Tecnai G2 F20) using a primary electron energy of 200 keV and Cs of 0.5 mm, energy-dispersive X-ray spectrometric (EDX) analysis conducted on a Link-ISIS-300 spectrometer, and N_2 adsorption-desorption measurements (Micromeritics ASAP 2002, USA). XPS measurements were obtained on a spectrometer (VG ESCA Lab 250) using Al K_α radiation and were deconvoluted using XPSPEAK software (Version 4.1).

It is well known that under acidic conditions above 80 °C, TAA undergoes slow hydrolysis to release H_2S , as expressed in Equation (1) [13]. The resulting H_2S molecules immediately react with the surrounding MoO_4^{2-} anions and H^+ cations to produce MoS_3 nanoparticles, as expressed in Equation (2) [16, 17]. The generated MoS_3 nanoparticles continuously diffuse into the pores of alumina where they deposit on the pore surface, forming an $\text{MoS}_3/\text{Al}_2\text{O}_3$ composite. MoS_3 species are very unstable in H_2 atmosphere at high temperature and are readily reduced into MoS_2 species [16–18], as shown in Equation (3), which renders MoS_3 species an excellent precursor of active phase MoS_2 . Therefore, $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalysts can be easily obtained by thermal treatment of $\text{MoS}_3/\text{Al}_2\text{O}_3$ composites in H_2 atmosphere.

Figure 1(a) shows the HRTEM image of the precursor EA- $\text{MoS}_3/\text{Al}_2\text{O}_3$ composite. The surface of alumina is coated with amorphous MoS_3 species, which was confirmed by EDX analysis [16–18]. However, once the precursor was heat-treated under H_2 , the resulting catalyst EA-Sul-CAT contained numerous dispersed MoS_2 nanocrystallites of uniform

Fig. 1. HRTEM images of the precursor EA-MoS₃/γ-Al₂O₃ composite (a) and the resulting MoS₂/Al₂O₃ catalyst (b).

size with suitable stacking on the surface of alumina, as shown in Fig. 1(b). Further analysis of the lamellar crystallites by HRTEM revealed that the interlamellar spacing was *ca.* 0.62 nm, indicating they are MoS₂ species [19]. The transformation of MoS₃ phases into MoS₂ ones was also demonstrated in S 2*p* XPS spectra and their fitting results obtained for EA-MoS₃/γ-Al₂O₃ and EA-Sul-CAT, as shown in Fig. S1 in the Supporting Information.

Table 1 lists the specific surface areas, pore volumes, and average pore diameters of the support and catalysts obtained by N₂ adsorption-desorption measurements. While both catalysts possess lower surface areas and pore volumes than the

Table 1

Textural properties of various samples.

Sample	$A_g^a/(m^2/g)$	$V_p^b/(cm^3/g)$	D_p^c/nm
γ-Al ₂ O ₃	215	0.51	9.8
EA-Sul-CAT	196	0.47	8.5
IM-CAT	178	0.40	7.8

^aBET surface area. ^bPore volume. ^cAverage pore diameter ($4V_p/A_g$).

γ-Al₂O₃ support, IM-CAT exhibits much larger decreases in surface area, pore volume and average pore diameter than EA-Sul-CAT because the formation of larger MoS₂ particles blocked the narrower pores of the support [6]. In contrast, EA-Sul-CAT prepared by ethanol-assisted chemical deposition has smaller MoS₂ particles that do not obviously affect the textural properties of the catalyst, as shown in the HRTEM images below.

Mo 3*d* XPS spectra of EA-Sul-CAT and IM-CAT and their deconvolutions are presented in Fig. 2. It is widely accepted [20–22] that the degree of sulfidation of Mo species, Mo_{sulfidation}, can be defined as the ratio of Mo⁴⁺ to the sum of Mo⁴⁺ and Mo⁶⁺, which can be calculated from deconvoluted XPS spectra; the results obtained are listed in Table 2. Mo_{sulfidation} is 96.8% for EA-Sul-CAT and only 67.1% for IM-CAT. Because Mo_{sulfidation} depends inversely upon the metal-support interaction, the higher Mo_{sulfidation} of EA-Sul-CAT suggests a weaker metal-support interaction than in IM-CAT [6,23], further proving that ethanol-assisted chemical deposition effectively avoids the formation of strong Al–O–Mo linkages. For IM-CAT, however, the strong interaction between Mo species and the γ-Al₂O₃ support results in incomplete sulfidation [10,11]. The unavoidable formation of bulk MoO₃ crystals and Al₂(MoO₄)₃ species further reduces the sulfidation of Mo species [24].

In addition to providing information on the degree of sulfidation, XPS has also been used to characterize the dispersion and accessibility of active sites to reactants in terms of the sur-

Table 2

XPS and HRTEM results for the catalysts.

Catalyst	Surface atomic ratio and degree of sulfidation		MoS ₂ morphology parameter	
	Mo _{sulfidation} (%)	Mo/Al	$\bar{L}/nm$	N
EA-Sul-CAT	96.8	0.186	3.3	3.0
IM-CAT	67.1	0.105	4.8	2.6

Fig. 2. Mo 3*d* XPS of EA-Sul-CAT (a) and IM-CAT (b).

Fig. 3. HRTEM images of EA-Sul-CAT (a) and IM-CAT catalysts (b).

face Mo/Al atomic ratio of catalysts [6,22,25]. The surface Mo/Al atomic ratios measured for EA-Sul-CAT and IM-CAT are listed in Table 2. Despite their identical metal content as determined by XRF, EA-Sul-CAT has a much higher surface atomic ratio than IM-CAT prepared by the conventional method, showing much higher dispersion and accessibility of the active sites to reactants. X-ray powder diffraction analysis of the catalysts (not shown) also indicated that EA-Sul-CAT contained well-dispersed Mo-based particles.

Figure 3 shows representative HRTEM micrographs of EA-Sul-CAT and IM-CAT, in which the black thread-like fringes correspond to MoS₂ slabs. Analyzing the statistical results of the length and stacking layer number distributions of MoS₂ slabs (not shown) revealed that in the EA-Sul-CAT catalyst, MoS₂ nanoslabs are well dispersed on the support with a much narrower size distribution and a higher stacking degree than those in sulfided IM-CAT. Moreover, Table 3 shows that the MoS₂ nanoslabs in EA-Sul-CAT have a smaller average length (3.3 nm) and a higher stacking degree (3.0 layers) compared with those in IM-CAT (4.8 nm and 2.6 layers, respectively). These results indicate that EA-Sul-CAT not only has more active sites exposed to reactants, but it also possesses higher intrinsic activity because of its more suitable stacking than that in IM-CAT [4,5].

DBT is a representative sulfur-containing compound found in petroleum and petroleum refining products and therefore was chosen to evaluate the performance of the HDS catalysts prepared in the present investigation. The HDS activities of the two sulfided Mo/ γ -Al₂O₃ catalysts, EA-Sul-CAT and IM-CAT, are shown in Table 3. The reaction rate constant (K_{HDS}), turnover frequency (TOF) and HDS ratio obtained over EA-Sul-CAT are all much higher than those over IM-CAT. By considering the characterization results, the difference between the HDS activi-

ties of the two sulfided catalysts can be explained as follows. On one hand, as mentioned above, EA-Sul-CAT contains better dispersed and more fully sulfided Mo species than IM-CAT, providing more active sites exposed to the reactants and thereby leading to the increased values of K_{HDS} and HDS ratio [1]. On the other hand, the strong interaction between the Mo species and alumina in IM-CAT prepared by conventional impregnation favored the formation of type I active sites with low intrinsic activity, whereas the weakened interaction between the Mo species and alumina in EA-Sul-CAT prepared by ethanol-assisted chemical deposition resulted in almost complete sulfidation of Mo species, generating more type II active sites with intrinsically high activity and thus giving a considerably higher TOF value [5]. Overall, the ethanol-assisted chemical deposition method we have developed produces catalysts with better dispersion and a higher degree of sulfidation of the active Mo species than those prepared by conventional methods. Both of these factors enhance the activity of catalysts prepared by ethanol-assisted chemical deposition.

HDS of DBT proceeds through two pathways: one is the direct desulfurization (DDS) route to produce biphenyl (BP), and the other is through hydrogenation (HYD) to form cyclohexylbenzene (CHB) with tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT) as intermediates [7]. The selectivity for various products and DDS/HYD ratios are given in Table 3. For the two catalysts studied, the preferential HDS route is DDS. The higher selectivity for BP and the much higher DDS/HYD ratio for EA-Sul-CAT compared with those for IM-CAT suggest the former has higher selectivity for DDS. The CHB selectivity over EA-Sul-CAT is much higher than that over catalyst IM-CAT, indicating the higher HDS activity of the former and revealing the potential of EA-Sul-CAT for deep HDS [6,7].

Table 3

DBT HDS activity and product selectivity over IM-CAT and EA-Sul-CAT.

Catalyst	K_{HDS}^a ($10^{-7} \text{ g}^{-1} \text{ s}^{-1}$)	TOF ^b (h^{-1})	HDS ratio ^c (%)	Product selectivity ^d (%)			
				THDBT+HHDBT	CHB	BP	DDS/HYD ^e
IM-CAT	0.18	0.27	88.9	60.9	15.4	23.7	0.31
EA-Sul-CAT	1.07	0.95	98.8	23.3	32.3	44.4	0.80
EF-Sul-CAT	0.10	0.25	85.6	—	—	—	—

^a HDS rate constant. ^b TOF is defined as the number of desulfurized DBT molecules per hour and per Mo atom on the edges of each MoS₂ crystallite. The calculation method was shown in the Supporting Information. ^c HDS ratios of DBT with LHSV of 20.0 h^{-1} . ^d Determined at about 50% of total DBT conversion by changing LHSV. ^e Obtained by dividing HYD into DDS, DDS = BP; HYD = CHB.

Fig. 4. HRTEM image of EF-Sul-CAT prepared by deposition without ethanol.

The above characterization and activity results show that the Mo species in EA-Sul-CAT possess higher dispersion, degree of sulfidation and HDS performance than those of IM-CAT. We noticed that ethanol plays an important role in tuning the size and morphology of the MoS₂ nanoparticles during their formation. Figure 4 shows a HRTEM image of EF-Sul-CAT prepared by chemical deposition without ethanol. Compared with EA-Sul-CAT prepared using ethanol, as shown in Fig. 1(b) and Fig. 3(a), the MoS₂ nanoparticles in EF-Sul-CAT possess much larger average length (7.8 vs. 3.3 nm) and much higher stacking (5.0 vs. 3.0 layers), illustrating the ability of ethanol to reduce the size of the precursor MoS₃ nanoparticles and their derived MoS₂ nanoparticles. Correspondingly, the larger size of the MoS₂ nanoparticles in EF-Sul-CAT resulted in fewer active sites, and thereby lower HDS activity, as shown in Table 3. The ethanol molecules help to disperse the precursor MoS₃ nanoparticles [14,26] because the S-rich surface of the MoS₃ nanoparticles may allow them to interact with ethanol molecules *via* “S...H-O” hydrogen bonds. Once MoS₃ particles form, ethanol molecules can be quickly adsorbed onto the surface of each particle, which may lessen their aggregation and help to control particle size.

In conclusion, we successfully developed an ethanol-assisted chemical deposition method to directly prepare sulfided Mo/Al₂O₃ HDS catalysts. Compared with the conventional impregnation method, our method produces catalysts

with higher dispersion and degree of sulfidation of active metal species, which greatly improves their HDS activity. In the preparation process, ethanol molecules disperse the precursor MoS₃ nanoparticles, helping to control the size of the active MoS₂ particles.

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Graphical Abstract

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Sulfided Mo/Al₂O₃ hydrodesulfurization catalyst prepared by ethanol-assisted chemical deposition method

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This communication presents a novel strategy to prepare a MoS₂/Al₂O₃ hydrodesulfurization (HDS) catalyst. The precursor MoS₃ was first synthesized using thioacetamide and sodium molybdate as sources of S and Mo, respectively, and ethanol as a dispersant. This precursor was then deposited onto the surface of a γ-Al₂O₃ support. The precursor was treated in H₂ atmosphere to obtain the MoS₂/Al₂O₃ HDS catalyst.

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乙醇辅助的化学沉积法制备硫化型Mo/ γ -Al₂O₃加氢脱硫催化剂

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摘要: 以硫代乙酰胺为硫源, 钼酸钠为钼源, 乙醇为分散剂, 采用化学沉积法制备了MoS₃/Al₂O₃催化剂前驱体, 再用H₂高温处理得到高分散硫化型MoS₂/ γ -Al₂O₃催化剂, 运用N₂吸附-脱附、X射线光电子能谱以及高分辨透射电子显微镜等技术对MoS₂/ γ -Al₂O₃催化剂进行了表征, 并以二苯并噻吩作为模型化合物评价了催化剂的加氢脱硫(HDS)活性。结果表明, 与浸渍法相比, 所制催化剂具有更大的比表面积和孔体积、更高的活性金属分散度、更佳的Mo物种硫化度以及更短的MoS₂片层长度和更高的堆积度, 因而在二苯并噻吩HDS反应中表现出远优于浸渍法所制催化剂的活性。乙醇可通过S...H-O氢键吸附至MoS₃纳米粒子表面, 可有效防止其生长和团聚, 起到分散剂的作用。

关键词: 加氢脱硫催化剂; 水解; 乙醇辅助; 三硫化钼; 二硫化钼

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加氢脱硫(HDS)是生产低硫清洁车用燃料最主要的手段, 开发高活性催化剂是提高HDS过程效率最经济有效的方法^[1]; 其中Mo/ γ -Al₂O₃催化剂是应用最为广泛的, 它的制备方法一直是HDS技术研发的焦点^[1,2]. 研究表明, 在Mo/ γ -Al₂O₃催化剂体系中, MoS₂微晶为催化剂活性相, 取决于其与载体Al₂O₃相互作用的强弱而呈现为两类结构: I型和II型^[2~5]. I型活性相具有高度分散的单层结构, 因与载体之间通过Mo-O-Al键相连, 具有较强的相互作用, 导致活性组分难以充分硫化, 活性较低; II型活性相具有多层堆积结构, 因与载体作用较弱, 利于活性组分充分硫化, 活性较高. 因此, 在实现金属活性组分高度分散的同时, 有效避免其与载体之间形成强相互作用进而促使其充分硫化是提升催化剂HDS性能的有效方法^[6].

商业上, 常以钼酸铵(AHM)为活性前体, 采用浸渍法引入活性组分, 以成型的Al₂O₃ (多为改性 γ -Al₂O₃的压出胶)为载体; 首先经浸渍、干燥、焙烧得到氧化型MoO₃/ γ -Al₂O₃催化剂, 再经硫化活化而制得催化剂^[2]. 研究表明^[7~9], Mo在浸渍液中主要以Mo₇O₂₄⁶⁻的形式存在, 该物种与Al₂O₃表面具有强烈的相互作用, 使得Mo在载体表面呈“蛋壳式”分布和过多的Al-O-Mo化学键的生成, 导致Mo物种难以被充分硫化, 进而形成过多低活性的I型活性相; 更为严重的是, Mo₇O₂₄⁶⁻会诱导Al₂O₃表

面解离产生Al³⁺, 随后与之反应形成Anderson型杂多阴离子Al(OH)₆Mo₆O₁₈³⁻, 其通过静电作用吸附至Al₂O₃表面, 再经焙烧生成大晶粒MoO₃和Al₂(MoO₄)₃物种^[10,11], 难以活化而不利催化剂活性的提高. 因此, 采用传统浸渍法制备的催化剂活性较低^[10]. 另外, 常规器内硫化氧化态HDS催化剂往往导致开工时间长, 装置腐蚀严重, 造成环境污染和人体伤害等问题^[12]. 因此, 近年来器外预硫化型HDS/加氢催化剂的开发和应用成为热点. 该催化剂的制备一般先将可溶性硫代钼盐或硫代钨盐等活性前体沉积至载体孔道中, 然后在惰性气体中进行热处理, 即得负载型硫化型催化剂^[13~15]. 然而, 这些制备方法仍处在实验室研究阶段.

因此, 本文提出一种直接制备硫化型MoS₂/Al₂O₃催化剂的路线, 即以硫代乙酰胺(TAA)为硫源, 利用其在低温、酸性条件下缓慢水解产生H₂S的特性, 通过液相沉积反应将MoS₃纳米颗粒负载于Al₂O₃载体表面, 并引入乙醇防止MoS₃颗粒的团聚, 首先制得催化剂前驱体MoS₃/Al₂O₃; 再在高温下用H₂还原, 从而制得硫化型催化剂MoS₂/Al₂O₃. 另外, 采用浸渍法制备了参比催化剂, 并运用高分辨透射电镜(HRTEM)、N₂吸附-脱附以及X-射线光电子能谱(XPS)等手段对两种催化剂进行了表征, 比较它们在二苯并噻吩(DBT) HDS反应中的催化性能.

配制30 ml Na₂MoO₄ (AR, 北京化学试剂公司)溶液

(0.2 mol/L), 然后按TAA:MoO₄²⁻摩尔比=3.3加入TAA (AR, 上海化学试剂公司), 搅拌下加入30 ml无水乙醇 (AR, 北京化学试剂公司), 将此体系转移至盛有3.0 g γ -Al₂O₃载体(20~40目, 工业级, 山东氧化铝厂)的100 ml反应釜中, 置于旋转烘箱中, 于84 °C处理24 h, 得到MoS₃/ γ -Al₂O₃, 记为EA-MoS₃/ γ -Al₂O₃, 其经洗涤、过滤后, 于50 °C真空干燥2 h和在500 °C于H₂气氛中处理4 h, 即得到硫化型催化剂MoS₂/ γ -Al₂O₃, 记为EA-Sul-CAT. 经X-射线荧光光谱(XRF, ZSX-11e型, Rigaku)测得该催化剂中的Mo的质量百分含量(以MoO₃计)为16.0%. 用30 ml去离子水代替30 ml无水乙醇, 同上法制备了硫化型催化剂EF-Sul-CAT.

与此同时, 采用传统浸渍法制备了具有相同Mo含量的催化剂. 具体制备过程为: 首先称取一定量的AHM (上海化学试剂公司), 配成溶液, 然后滴加2.4 mol/L的HCl至pH=4.5, 再加入定量 γ -Al₂O₃, 浸渍至少12 h后, 于110 °C干燥10 h, 500 °C焙烧4 h, 得到氧化型催化剂MoO₃/ γ -Al₂O₃. 然后采用含3%CS₂的环己烷溶液为硫化剂, 在300 °C、4.0 MPa、液时体积空速(LHSV) 8.0 h⁻¹、H₂/Oil体积比400的条件下硫化5 h, 得到硫化态催化剂, 记为IM-CAT.

使用荷兰Philips公司生产的Tecnai G2 F20型场发射透射电子显微镜(最高加速电压为200 kV, Cs为0.5 mm, 同时配有Link-ISIS-300型X射线能谱分析仪(EDX)获取前驱体和催化剂的HRTEM照片. 在美国Micromeritics公司生产的ASAP 2002型物理吸附仪上对样品进行N₂吸附-脱附表征. 在英国VG公司生产的ESCA Lab 250型X射线光电子能谱仪上对催化剂进行XPS表征, 通过XPSPEAK 4.1软件对Mo3d XPS谱图进行拟合分析.

研究表明, 在酸性溶液中在80 °C以上时TAA会缓慢水解产生H₂S (见式(1)); 后者随即与周围的MoO₄²⁻和H⁺发生晶化成核反应, 生成MoS₃纳米粒子沉淀 (见式(2))^[16,17]; 所形成的MoS₃纳米粒子经扩散、沉积至 γ -Al₂O₃孔道中, 得到MoS₃/Al₂O₃催化剂前驱体^[13]. 同时, MoS₃在H₂中发生反应生成MoS₂ (见式(3))^[16~18]. 为此, 我们将催化剂前体EA-MoS₃/Al₂O₃置于H₂气氛中, 于500 °C处理4 h后得到了硫化型催化剂MoS₂/Al₂O₃, 即EA-Sul-CAT.

图1为未经处理的EA-MoS₃/ γ -Al₂O₃样品和在高温

H₂中处理后的EA-Sul-CAT样品的HRTEM照片. 可以看出, 未经处理的样品呈无定形态, 这与MoS₃的无定形结构有关^[16~18]; 经高温H₂处理后, 在 γ -Al₂O₃载体表面形成了数目较多的尺度细小、分布均匀、呈片层堆垛结构的MoS₂纳米微晶; 测得两相邻片层的层间距约为0.62 nm, 表明所形成的硫化物活性相为MoS₂物种^[19]. 同时, 通过对比EA-MoS₃/ γ -Al₂O₃和EA-Sul-CAT样品的S 2p XPS谱图以及相应的拟合图也可以有效证明由MoS₃至MoS₂的相变过程(详见支撑材料中的图S1).

表1为EA-Sul-CAT和IM-CAT样品的比表面积和孔结构数据. 由表可见, 当所用载体和活性组分的负载量相同时, EA-Sul-CAT催化剂具有更大的比表面积、孔体积和平均孔径. 这是由于乙醇辅助的化学沉积法可以获得颗粒尺寸细小、均匀的Mo物种, 其对载体孔结构的影响较小; 而常规浸渍法所得的Mo物种颗粒尺寸较大, 且其分布不均匀, 很容易堵塞Al₂O₃中的部分窄孔道, 导致催化剂的比表面积、孔体积以及平均孔径与载体的相比均明显降低^[6].

图2为上述催化剂的Mo 3d XPS谱及根据不同化学价态的Mo的结合能进行拟合得到的XPS谱图. 根据拟合结果, 以Mo⁴⁺/(Mo⁴⁺+Mo⁶⁺)表示Mo的硫化度(Mo_{sul})^[20~22], 其值列于表2中. 由表可知, EA-Sul-CAT的Mo_{sul}高达96.8%, 而IM-CAT的仅为67.1%, 表明前者中形成了较多的高活性MoS₂物种. 这是由于EA-Sul-CAT样品中较弱的金属-载体相互作用所致, 表明乙醇辅助的化学沉积法可有效避免Al-O-Mo化学键的生成, 从而削弱了金属与载体间相互作用^[6,23]. 而IM-CAT催化剂中金属-载体相互作用较强, 从而导致金属活性组分硫化困难^[10,11]; 另一方面, 在制备过程中形成了一定量的大颗粒MoO₃物种和Al₂(MoO₄)₃复合物, 两者均难以被充分硫化^[24].

XPS除被用于测定催化剂活性组分的硫化度外, 还可以获取催化剂表面的Mo/Al原子比, 进而用来描述活性组分的分散度和活性中心的可接近性^[6,22,25]. 催化剂表面Mo/Al原子比列于表2中. 可以看出, EA-Sul-CAT表面的Mo/Al原子比高达0.186, 远高于IM-CAT的0.105, 表明前者具有更高的活性组分分散度和更佳的活性中心可接近性. 此外, 通过X射线粉末衍射(XRD)分析也表明所制催化剂具有优异的分散度(详见支撑材料中的图S2).

图3为EA-Sul-CAT和IM-CAT催化剂HRTEM照片. 结合样品中MoS₂片晶长度和层数的统计分布图(见支撑

材料中图S3)可知,在EA-Sul-CAT中,MoS₂片晶尺寸较小,在载体上分散均匀,且堆积度高;而在IM-CAT中MoS₂片晶尺寸较大、分布较宽,在载体上分散不均匀,大多为单层堆垛。表2列出了这两个催化剂中MoS₂片晶长度和堆垛层数的统计结果。由表可见,在EA-Sul-CAT中的MoS₂片晶平均长度为3.3 nm,平均堆垛层数达到3.0,而在IM-CAT中的分别为4.8 nm和2.6层,这充分表明在EA-Sul-CAT中活性相不仅可以暴露更多的活性位以充分接触反应物分子,而且因其较高的堆积度而拥有更高的内在活性^[4,5]。

以DBT作为模型化合物评价了EA-Sul-CAT和IM-CAT催化剂的HDS反应性能,结果列于表3。可以看出,EA-Sul-CAT的 K_{HDS} 和TOF分别是后者的6倍和近4倍,脱硫率也远远高于后者。

比较而言,EA-Sul-CAT中活性相呈高度分散状态,粒径更小,硫化得更完全,因而有更多的活性中心^[1],所以催化剂的 K_{HDS} 和脱硫率更高。另一方面,EA-Sul-CAT中活性组分-载体相互作用较弱,使活性金属组分的硫化度较高,从而形成更多的II型活性中心,因此TOF值较高^[5]。总之,采用乙醇辅助的化学沉积法不仅可以保证催化剂具有优异的活性组分分散度,而且可以大幅增加活性组分的硫化还原能力,最终使催化剂具有优异的HDS性能。

DBT在Mo/Al₂O₃催化剂上发生的HDS反应主要通过两种路径进行:(1)DBT氢解直接脱硫(DDS)生成联苯(BP);(2)DBT预加氢(HYD)生成环己基苯(CHB)以及中间产物四氢二苯并噻吩(THDBT)和六氢二苯并噻吩^[7]。不同产物的选择性以及DDS/HYD比值列于表3中。可见,两个催化剂上的BP选择性均高于CHB,表明HDS

反应均以DDS路径为主。比较而言,EA-Sul-CAT上BP选择性和DDS/HYD比值更高,即DDS反应活性更佳。且,CHB选择性也更高,因而表现出更优的HYD反应活性,从而拥有潜在的深度HDS能力^[6,7]。

综上所述,乙醇辅助的化学沉积法可明显改善活性组分Mo物种的分散状态和硫化程度,调控活性相的微观形貌,进而显著提高其HDS活性。图4给出了不加乙醇时采用乙醇辅助的化学沉积法制备的EF-Sul-CAT催化剂的HRTEM照片。由图可见,活性相MoS₂粒子以较大的尺度零星地分散在载体表面,且堆积度很高。统计分析表明,EF-Sul-CAT样品中MoS₂颗粒的平均长度高达7.4 nm,平均堆垛高度达到5.0层。由此不难推断,活性相前驱体MoS₃颗粒尺度过大,导致活性相MoS₂尺度过大,使得处于活性相片晶边缘位的Mo原子数目较少,致使催化剂的 K_{HDS} ,TOF和脱硫率均较低(见表3)。结合上文可知,向化学沉积体系中添加乙醇可有效控制所生成的活性前体MoS₃的尺度。可见,乙醇起到MoS₃颗粒分散剂的作用。研究表明,MoS₃纳米粒子表面为富S结构,其与乙醇分子间具有键合效应,二者可通过氢键S...H-O紧密结合;MoS₃成核后,其周围的乙醇分子很快通过氢键作用将其包覆,从而有效地抑制其生长和团聚,起着分散剂的作用^[14,26]。

综上所述,本文提出了一种直接制备硫化型Mo/Al₂O₃催化剂的乙醇辅助的化学沉积制备方法。实验结果表明,与浸渍法相比,采用该法制备的催化剂不仅具有更高的Mo物种硫化度和分散度,还具有长度更短、堆积度更高的MoS₂形貌,在DBT的HDS反应中表现出更高催化性能。在制备过程中,添加的乙醇起到分散剂的作用。