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Manuscript Draft

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Title: Tailoring the structure of Co-Mo/mesoporous γ-Al2O3 catalysts by adding multi-hydroxyl compound: A 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization study

Article Type: SI:ISCRE 25

Keywords: hydrodesulfurization; diesel; structure manipulation; Co-Mo/mesoporous Al2O3; industrial-scale

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First Author: Chong Peng

Order of Authors: Chong Peng; Rong Guo; Xiang Feng; xiangchen fang, Prof. Dr.

Abstract: Ever-increasing concern on environmental impacts (e.g., sulfur pollution) by fossil fuels has triggered the research on hydrodesulfurization (HDS). In this work, Co-Mo nanoparticles were deposited on the mesoporous γ-Al2O3 support with the addition of organic compound, and the physico-chemical properties of the catalysts (Co-Mo-C/mesoporous γ-Al2O3) were then characterized by multi-techniques such as H2-TPR, HRTEM, XPS, N2 physisorption. It is found that the Co-Mo-C/mesoporous γ-Al2O3 catalyst is easier to be reduced when organic compound is added, enhancing the sulfuration. This results in better dispersion of Co-Mo-S species and more Co-Mo-S II active sites, which significantly enhance diesel ultra-deep hydrodesulfurization activity. Furthermore, this novel catalyst was also tested for HDS reaction in a 3000 kt/a industrial-scale plant. Gratifyingly, this catalyst showed effective reduction of sulfur content from 9000 to less than 10 μg/g and also high stability over 5000 h. The results are of great significance to the design and development of industrial HDS catalysts.

Response to Reviewers: Thank you very much for your valuable comments and suggestions. We tried our best to improve the manuscript and made the changes in the revised version. We hope that the corrections will meet with approval.

Reviewer #1:
Controlling and decreasing the environmental impacts of fossil fuels on the environment and human shows great scientific and industrial importance. This paper deals with the quite essential topic of eliminating sulfur heteroatom in fossil fuels processing.
The authors developed the multi-hydroxyl compound promoted Co-Mo/Al2O3 catalyst, and elucidated the effect of multi-hydroxyl compound on catalyst structure and performance for diesel ultra-deep hydrodesulfurization. The characterizations and discussions convincingly demonstrate the structure-performance relationship. Moreover, the

promoted catalyst can be even used in 3000kt/a industrial process, which is of great referential significance to the design of other HDS catalysts. Therefore, this paper is written in good English and can be accepted for publication after the following revision.
Response:
Thanks for the good comments on the quality of our manuscript.

1) For diesel HDS catalyst, the pore structure of support should also be essential to the catalytic performance. Please add discussion on the role of support in HDS reactions to better improve this paper.
Response:
It is true as the reviewer mentioned that pore structure of support is essential.
In order to better improve this paper, we added the following discussion in the revised manuscript: "Al2O3 in α and γ forms is the most common support for HDS catalysts because of its outstanding textural and mechanical properties. Normally, these properties can be easily tuned based on the detailed reaction requirements, feedstock compositions and product's targeted specifications." and "Among the structural and textural properties, pore size is extremely essential because the diffusion of different species inside pores of Al2O3 could affect and limit the HDS overall reaction rate".

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Thanks for the careful review by the reviewer. The new figure 1 with high resolution has been added in the revised manuscript.

Reviewer #2:
This article described a novel method to tailor the micro-structure and catalytic performance of diesel HDS catalysts via the addition of glycerol into the impregnation solution. Interestingly, the authors found that this simple method could lead to the fine tuning of the

resulting Co-Mo-S active phase in terms of slab size and dispersion, and accordingly the catalyst prepared with the addition of glycerol exhibited much better catalytic performance in diesel HDS. More importantly, the authors demonstrated that the resulting catalyst has been commercially used for 3 years in a 3000 kt/a industrial unit. I recommend this article for publication in CEJ after the following revisions in addition to those I have marked in the pdf document:
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SINOPEC Dalian Institute of Petroleum and Petrochemicals

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Dear Prof. Enrico Tronconi,

On behalf of my co-authors, we thank you very much for your efforts in our manuscript and the minor revision decision. We also appreciate the reviewers very much for their constructive comments and valuable suggestions on our manuscript entitled "*Tailoring the structure of Co-Mo/mesoporous γ-Al_2O_3 catalysts by adding multi-hydroxyl compound: A 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization study*". (ID: CEJ-D-18-06459).

We have studied reviewers' comments carefully and have made all revisions required by reviewers. Attached please find the revised version, which we would like to submit for your kind consideration. Looking forward to hearing from you.

Thank you and best regards.

Sincerely yours

Xiangchen Fang

List of potential reviewers:

1) **Prof. Xiaojun Bao**

Fuzhou University, Fujian, China

E-mail: baoxj@fzu.edu.cn

Prof. Bao is an expert in hydrodesulphurization catalysis. His review will be helpful to improve the quality of the paper.

2) **Prof. Jinsen Gao**

State Key Laboratory of Heavy Oil Processing, Beijing, China

E-mail: jsgao@cup.edu.cn

Prof. Gao is an expert in hydrotreating of fuel and has published many papers in related research field.

3) **Prof. Zhigang Lei**

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, China

E-mail: leizhg@mail.buct.edu.cn

Prof. Lei is an expert in sulfur removal and published many papers in this research field.

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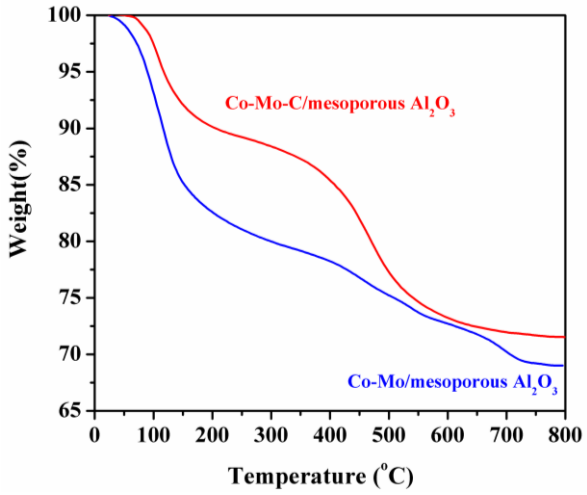

Figure 1. TGA results of Co-Mo/Mesoporous Al_2O_3 and Co-Mo-C/Mesoporous Al_2O_3 catalysts.

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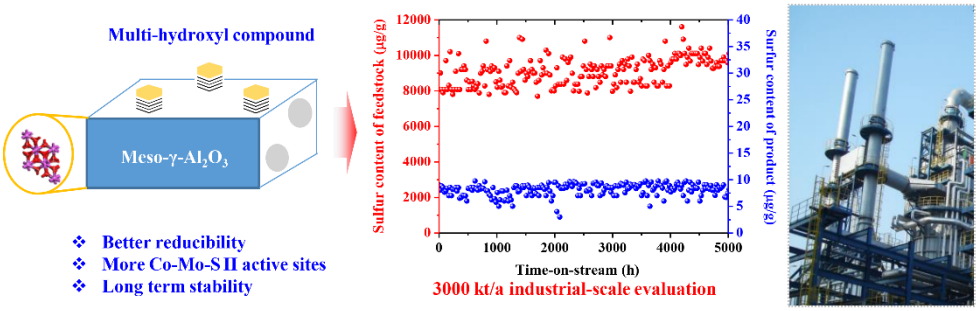
Graphical abstract:



Highlights:

- Co-Mo nanoparticles are impregnated with the addition of multi-hydroxyl compound.
- Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is easier to be reduced.
- More Co-Mo-S type II sites exist due to weak metal-support interaction.
- 99.9% sulfur removal activity is achieved over 5000 h in a 3000kt/a industrial plant.

Supplementary Material

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Tailoring the structure of Co-Mo/mesoporous γ-Al_2O_3 catalysts by adding multi-hydroxyl compound: A 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization study

Chong Peng[†], Rong Guo[†], Xiang Feng[*‡] and Xiangchen Fang[*†]

[†] Dalian Research Institute of Petroleum and Petrochemicals, SINOPEC, Dalian 116045, China

[‡] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China

Abstract: Ever-increasing concern on environmental impacts (e.g., sulfur pollution) by fossil fuels has triggered the research on hydrodesulfurization (HDS). In this work, Co-Mo nanoparticles were deposited on the mesoporous γ-Al_2O_3 support with the addition of organic compound, and the physico-chemical properties of the catalysts (Co-Mo-C/mesoporous γ-Al_2O_3) were then characterized by multi-techniques such as H_2-TPR, HRTEM, XPS, N_2 physisorption. It is found that the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is easier to be reduced when organic compound is added, enhancing the sulfuration. This results in better dispersion of Co-Mo-S species and more Co-Mo-S II active sites, which significantly enhance diesel ultra-deep hydrodesulfurization activity. Furthermore, this novel catalyst was also tested for HDS reaction in a 3000 kt/a industrial-scale plant. Gratifyingly, this catalyst showed effective reduction of sulfur content from 9000 to less than 10 μg/g and also high stability over 5000 h. The results are of great significance to the design and development of industrial HDS catalysts.

Keywords: hydrodesulfurization; diesel; structure manipulation; Co-Mo/mesoporous Al_2O_3; industrial-scale

1. Introduction

Growing concern on environment necessitates the elimination of heteroatoms such as sulfur and nitrogen from fossil fuels. This worldwide demand for clean fuels leads to strict legislation to control and decrease the environmental impacts of fossil fuels on the environment and human beings. For example, Euro V standard of diesel fuel strictly requires that the diesel sulfur content is less than 10 ppm[1]. However, the removal of refractive sulfur-containing alkyl derivatives of dibenzothiophene (DBTs)[2], such as 4-dimethyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), is quite challenging. Ultra-deep hydrodesulfurization (HDS) to produce ultra-low-sulfur[3] diesel fuels with sulfur content of less than 10 ppm is one of the most essential industrial processes to resolve the above problem[4-6]. This has triggered the great attention of researchers on developing highly efficient catalysts for HDS [7-11].

The most important HDS catalyst used in oil refineries is usually the Co(Ni)Mo/Al_2O_3 catalysts [12-14]. The structure of the typical Co(Ni)-Mo catalyst can be briefly described by the Co(Ni)-Mo-S model, which was first reported by Topsøe[15] The structure of catalytically active Co(Ni)-Mo-S sites is formed by the decoration of Co(Ni) atoms on the well-dispersed MoS_2 nanocrystals[16]. These active sites can be obtained by the sulfidation process[3]. It is widely accepted that the HDS activity and stability of the catalysts are greatly affected by the physico-chemical properties of the support and metals [1, 2]. Al_2O_3 in α and γ forms is the most common support for HDS catalysts because of its outstanding textural and mechanical properties. Normally, these properties can be easily tuned based on the detailed reaction requirements, feedstock compositions and product's targeted specifications[17].

Besides the properties of support, the interaction between the support and Co-Mo metals are usually quite essential to the design of effective HDS catalyst. It was reported that using chelating agents or additives such as P and B can reduce the interaction between active metals and aluminum supports, producing more active HDS sites [18-20]. Although much attention has been devoted to understanding the effect of support properties on HDS performance, few reports were focused on enhancing catalytic performance by manipulating the metal-support interaction aiming at industrial application. There is urgent need to design suitable catalyst for industrial HDS reaction, which is of prime scientific and industrial importance.

In this work, the effects of organic compound on catalyst structure and HDS performance are investigated, aiming at the industrial-scale HDS process development. Mesoporous γ-Al_2O_3 is first employed as support, and then load Co-Mo nanoparticles with the addition of organic compound. The physico-chemical properties of the catalysts are studied by multi-techniques such as XRD, XPS, TPR, HRTEM, NH_3-TPD and Py-IR. It is found that the introduction of organic compound makes the catalyst easily reduced, generating more type II Co-Mo-S active sites and enhancing the HDS activity and stability. Moreover, this catalyst is also tested in an 3000 kt/a industrial-scale HDS unit, and shows fantastic 99.9% sulfur reduction from 9000 to less than 10 μg/g over 5000 h. The properties of the used catalyst after long-term evaluation and regeneration are further discussed. The results reported herein are of great referential importance to the design of industrial catalysts, and is expected to be extended to other HDS catalysts.

2. Experimental

2.1 Synthesis of Co-Mo/mesoporous γ-Al_2O_3 catalyst

The mesoporous γ-Al_2O_3 support was provided by Fushun Catalysts Factory of

SINOPEC. Two Co-Mo catalysts were prepared by impregnation with an aqueous solution of cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$] and ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] with and without the addition of multi-hydroxyl compound. The loadings of Mo and Co oxides are 18 and 3wt%, respectively. The resultant catalysts were then dried at 110 ^oC and calcined at 500 ^oC for 3 h. The catalysts were then subjected to sulfidation. Typically, the catalyst was placed in a reactor at 4 MPa of H_2 and heated to 110 ^oC. Sulfidizing oil (96% kerosene and 4% CS_2) was then added into the reactor and maintained for 3 h. Afterwards, the reactor was heated to 360 ^oC for 8 h. The resultant catalyst prepared with the addition of multi-hydroxyl compound is named as Co-Mo-C/mesoporous γ-Al_2O_3. For comparison, the catalyst without multi-hydroxyl compound addition is denoted as Co-Mo/mesoporous γ-Al_2O_3.

2.2 Characterizations

N_2 physisorption was performed on a Micromeritics ASAP 2020 instrument at -196 ^oC. Each sample was heated to 300 ^oC under vacuum for 3 h prior to testing. The XRD patterns of the catalysts were determined on a Rigaku Miniflex powder diffractometer with CuK_α radiation (λ=0.154 nm). TPR curves were obtained on a Micromeritics AutoChem 2920 instrument to analyze the reducibility of the catalysts. All samples were calcined at 450 ^oC for 1 h and then heated from room temperature to 1000^oC in a 10% H_2/Ar mixture. XPS were performed on a Multilab2000X instrument (ThermoFisher) using Mg-K_α radiation. All spectra were corrected using 284.6 eV as the reference for C1s binding energy. HRTEM measurements were conducted on a JEM-2100 instrument operating at 200 kV. The sulfur content was obtained by sulfur content analysis (ANTEK-9000) using Ar and O_2 as carrier and burning gas, respectively. The analysis standard was SH/T0689-2000. NH_3-TPD was conducted as follows: the catalysts after calcination were saturated with NH_3 for 30 min at 100^oC. Afterwards, He

was flushed to remove the physically adsorbed molecules. The TPD results were collected in He from 323 to 873 K with a heating rate of 10 K/min. Py-adsorbed IR spectra were recorded on a PE FTIR Frontier instrument. The system was degassed at 500 ^{o}C for 5 h under vacuum and flushed by pure pyridine at room temperature for 20 min. The infrared (IR) spectra were then recorded.

2.3 Catalytic testing in a 3000 kt/a industrial unit

The industrial-scale HDS reaction was carried out in a fixed bed reactor, and the corresponding schematic diagram is illustrated in Fig. 1. Typically, Co-Mo-C/mesoporous γ-Al_2O_3 catalyst was shaped into particle with size of 1-3 mm. Both the top and bottom of the fixed bed reactor were filled with inert particles. The catalysts were loaded into reactor of D/d_p > 18, L/d_p >350, where D, L and d_p are the inner diameter, height of bed and catalysis particle size, respectively. The feedstock was pumped into the furnace, and was heated first through heat exchanger. The heated feedstock was then introduced into the reactor. After reaction, the final products were separated by high-pressure and low-pressure separators.

(Figure 1 should be inserted herein)

3. Results and discussions

3.1 Effect of organic compound on catalyst structure

The mesoporous γ-Al_2O_3 support in this work was first characterized by N_2 physisorption, as shown in Fig. 2a. According to the IUPAC classification, it can be seen that this support has Type IV adsorption-desorption isotherms[1, 21], revealing the mesoporous characteristic. The hysteresis loop of the isotherm starts at ~0.4, indicating that the mesopores are intracrystalline rather than intercrystalline. From the inset of Fig.

2a, it is observed that the mesoporous γ-Al_2O_3 support has average pore size (ca. 7.8 nm). The detailed information of pore structure is summarized in Table S1. The pore volume and surface area of mesoporous γ-Al_2O_3 support are normally larger than those of a typical commercial Al_2O_3 support. Among the structural and textural properties, pore size is extremely essential because the diffusion of different species inside pores of Al_2O_3 could affect and limit the HDS overall reaction rate. It is reported that the size of 4,6-DMDBT molecules estimated by molecular orbital calculations is 0.59 × 0.89 nm[22]. This pore size is favorable for the diffusion of the sulfur-containing alkyl derivatives of dibenzothiophene. Based on this mesoporous γ-Al_2O_3 support, Co-Mo nanoparticles are deposited on support with the addition of the compound. To better show the role of the compound, Co-Mo/mesoporous γ-Al_2O_3 catalyst without the addition of compound is compared. Fig. 2b shows the XRD patterns of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst. Both of the two samples exhibit intense peaks at 46^o and 66.8^o, which are correlated to the planes (100) and (110) of the γ-Al_2O_3 phase (JCPDF#29-0063)[23], respectively. There is no low-intensity broad peaks between 16^o and 32^o, indicating the absence of amorphous Al_2O_3 phase. For Co-Mo/mesoporous γ-Al_2O_3 catalyst, there is a peak at 26^o which is related to the MoO_3 (021) species. In comparison, no peak shows up at 26^o for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst, indicating that the particles are well-dispersed on support.

(Figure 2 should be inserted herein)

Acidity of a catalyst is a key parameter affecting the HDS performance[24]. For the mesoporous γ-Al_2O_3 support, there are three kinds of NH_3-TPD peaks corresponding to different strengths, i.e., weak acidity (150-250^{o}C), medium acidity (250-450^{o}C) and strong acidity (>450^{o}C) [25, 26]. The total acid content includes 36.0% weak acidity,

64.0% medium acidity and 0% strong acidity. The total acid content of mesoporous γ-Al_2O_3 support is 0.654 mmol/g. After loading CoMo nanoparticles, the Lewis and Brönsted sites of the two catalysts are determined by Py-IR. The bands at 1445 and 1556 cm^{-1} are attributed to the pyridine chemisorbed on Lewis sites and the vibration mode of pyridinium ion adsorbed on Brönsted sites, respectively[27]. In addition, the pyridine adsorbed on both Lewis and Brønsted sites show up at 1486 cm^{-1}. The numbers of sites and B/L ratio of the two catalysts are listed in Table 1. It can be seen from Table 1 that total acid sites together with B/L ratio are all larger on Co-Mo-C/mesoporous γ-Al_2O_3 than those on Co-Mo/mesoporous γ-Al_2O_3 catalyst, possibly due to the formation of complex between metal and multi-hydroxyl compound. This could greatly affect the HDS reaction. It is reported that higher total acidity with larger B/L ratio could enhance the HDS performance [28]. Therefore, the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is expected to show better HDS activity.

(Table 1 should be inserted herein)

The interaction between metal and support is then investigated by H_2-TPR, which is a powerful technique to investigate the reduction behavior of supported phases. Fig. 3 shows the H_2-TPR spectra of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts. According to Moulijn et al.[29], there is a reduction peak of well-dispersed molybdenum supported species at low temperature of ca. 450°C. This is attributed to the partial reduction of Mo(VI) to Mo(IV) of amorphous, highly defective, multilayered oxides (octahedral Mo species) bounded to Al_2O_3 support[30, 31]. It is clear that the intense peak for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is located at 445°C, which is lower than 462.7°C for Co-Mo/mesoporous γ-Al_2O_3 catalyst, demonstrating that the interaction between metal and support is weak for Co-Mo-

C/mesoporous γ-Al_2O_3 catalyst. This weak interaction is reported to be beneficial to the catalytic performance of HDS reaction due to the formation of Co-Mo-S type II sites[2]. Moreover, the absence of additional reduction peaks at 350 ◦C indicate that Co oxide supported crystallites is not formed on the supports.

(Figure 3 should be inserted herein)

To obtain information regarding the morphology and distribution of Co-Mo-S crystallites, the two catalysts are then analyzed by HRTEM, and the typical HRTEM images are shown in Fig. 4. Due to the good dispersion of Co, the Co nanoparticles can not be observed by HRTEM characterization[32]. This is also in accordance with the XRD results in Fig. 2b. The black thread-like fringes are the Co-Mo-S phase. The average Co-Mo-S slab length (L) can be calculated from the following equation (3-1):

$$\bar{L} = \frac{\sum_{i=1}^{n} n_i l_i}{\sum_{i=1}^{n} n_i} \qquad (3\text{-}1)$$

where l_i is the length of *i*th slab, n_i is the number of particle with a l_i length. The statistical results of the length and stacking distributions of Co-Mo-S for the two catalysts are shown in Table 2. Maximum slab length of Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is smaller, and the average length of the slabs on Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is 4.8 nm, shorter than the 9.5 nm for Co-Mo/mesoporous γ-Al_2O_3 catalyst. In addition, the percentages of Co-Mo-S slabs with 1-2 layers are 75.2 and 47.9% for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts, respectively. The percentages of 3-5 layers of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are 20.1 and 49.7%, respectively. The results show that the addition of compound decrease the interaction between metal and support. Therefore,

the average length reduces and the dispersion increases. Moreover, it is reported that the phase with 3-5 layers is Co-Mo-S type II, which could exhibit superior HDS performance than Co-Mo-S type I (1-2 layers)[33].

(Figure 4 should be inserted herein)

(Table 2 should be inserted herein)

The surface concentrations of Mo in multiple oxidation states, and the binding energies of Co and Mo can be determined by XPS, as shown in Table 3. The catalysts are stored in nitrogen before XPS test to prevent the re-oxidation by air. The typical curve-fitting of Mo 3d is shown in Fig. S1. The Mo 3d spectra can be divided into three sets of doublets, which correspond to the Mo^{4+}, Mo^{5+} and Mo^{6+} species[2]. The Mo^{4+} species is usually MoS_2, which is usually regarded as the active phase[28]. The Mo^{5+} and Mo^{6+} species can be attributed to Mo oxy-sulfide and not completely sulfided Mo species, respectively. From Fig. S1 and Table 3, it is seen that the percentage of Mo^{4+} in the sum of Mo^{4+}, Mo^{5+} and Mo^{6+} species is 75.03% for Co-Mo-C/mesoporous γ-Al_2O_3. In comparison, this value for Co-Mo/mesoporous γ-Al_2O_3 catalyst is only 65.88%. In addition, it is also noticed that the Mo binding energy for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is also lower than that for Co-Mo/mesoporous γ-Al_2O_3 catalyst. The lower binding energy and higher percentage of Mo^{4+} all suggest that the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst has weaker interaction between metal and support, and thus is more easily sulfided, leading to more Co-Mo-S active phases. This finding is also in accordance with the finding of H_2-TPR (Fig. 3) and HRTEM (Fig. 4) results.

(Table 3 should be inserted herein)

3.2 Catalytic performance of Co-Mo-C/mesoporous Al_2O_3 catalyst

The Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are then tested for HDS reaction. The properties of the testing diesel oil are shown in Table 4. The sulfur content for this diesel oil is 9000 $\mu g \cdot g^{-1}$. From table 4, it is seen the diesel has high sulfur and low nitrogen content, high 95% and FBP, indicating the difficulty of HDS. The HDS results at different temperature for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are summarized in Table 5. At 360^oC, 6.0 MPa (H_2 pressure) and 0.77 h^{-1}, Co-Mo/mesoporous γ-Al_2O_3 catalyst shows poor HDS performance with the product sulfur content of 12 $\mu g \cdot g^{-1}$. In contrast, the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst has better performance. The low sulfur content of 7.4 $\mu g \cdot g^{-1}$ meets the requirement of Euro V standard. Further increasing the reaction temperature leads to reduced sulfur contents. The values for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are 7.0 and 4.0 $\mu g \cdot g^{-1}$, respectively. Therefore, the temperature for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst could be 10^oC lower than that for Co-Mo/mesoporous γ-Al_2O_3 catalyst, which could greatly reduce the energy consumption.

(Table 4 should be inserted herein)

(Table 5 should be inserted herein)

From the above results, the main reasons for the enhanced performance for Co-Mo-C/mesoporous γ-Al_2O_3 support could be the more active Co-Mo-S type II species, which are originated from weak interaction between metal and support. The higher activity of Co-Mo-S Type II is generally associated to the high staking number of slabs bonding weakly to the support through a small Mo-O-Al linkage[34]. Moreover, it is also reported that the normal HDS reaction routes[28] include hydrogenation, direct hydrogenolysis and alkyl transfer desulfurization. Higher B/L ratio and presence of Co-Mo-S type II species may also lead to better alkyl transfer desulfurization of refractory

sulfides such as 4, 6-DMDBT[23, 28]. The ultradeep hydrodesulfurization performance of Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is compared with reported catalysts. It can be seen in Table 6 that the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst shows a high activity compared to catalysts reported in the literature[10, 34-38].

(Table 6 should be inserted herein)

It has been confirmed that Co-Mo-C/mesoporous γ-Al_2O_3 catalyst has enhanced performance for HDS reaction. To further verify the stability of this catalyst, the long-term stability is subsequently evaluated in industrial-scale 3000kt/a plant. The reaction conditions and results are shown in Table 7 and Fig. 5. The HDS reaction works at low H_2 pressure P=5.9 MPa, inlet temperature T_i=350^{o}C, outlet temperature T_o=362^{o}C, average temperature T_a=358^{o}C, hydrogen to oil ratio=308 and space velocity V=0.70h^{-1}. Clearly, the industrial evaluation of Co-Mo-C/mesoporous γ-Al_2O_3 catalyst also meets the Euro V requirement of diesel with low sulfur content of 7.8 μg·g^{-1}. The long-term evaluation of catalyst at the same reaction condition is shown in Fig. 5. The catalyst maintains high stability with the low product sulfur content (i.e., smaller than 10 μg·g^{-1}) over 5000 h. The reason for the good catalytic stability should be the enhanced mass transfer ability together with the unique structure of active Co-Mo-S sites.

(Table 7 should be inserted herein)

(Figure 5 should be inserted herein)

It should be noted that the coke formation on Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is inevitable due to the contact with carbonaceous feedstock during the long-term stability test. Therefore, the reaction temperature is normally increased by ca. 0.5^{o}C/month to maintain the quality of products. After long running time, the catalyst

should be regenerated. The fresh, used and regenerated catalysts in air at 420^{o}C are then characterized by N_2 physisorption. Fig. 6 shows that all of the three samples show similar type IV adsorption-desorption isotherms. The hysteresis loop of the isotherm for the samples all start at ca. 0.4, indicating that the mesoporous structure is well maintained. The pore volume of the fresh catalyst is 0.33 cm^3/g, which decreases to 0.19 cm^3/g after long-term testing. The regeneration successfully removes the carbonaceous deposits inside the pores, and increases the pore volume from 0.19 cm^3/g to 0.33 cm^3/g, which is almost the same to fresh catalyst. By using this catalyst, the 3000 kt/a industrial plant in China with the catalyst technique from SINOPEC has been running smoothly for 3 years. After 3 years, the regenerated catalyst also shows good HDS performance (Table S2-3). This Co-Mo-C/mesoporous γ-Al_2O_3 catalyst shows good performance with the reduced reaction temperature, saving the energy consumption and greatly increasing the profit. This catalyst is also of referential importance to the design of industrial catalyst for diesel ultra-deep hydrodesulfurization.

(Figure 6 should be inserted herein)

4. Conclusion

In this work, hydrodesulfurization reaction catalyzed by Co-Mo-C/mesoporous γ-Al_2O_3 catalyst at 3000 kt/a industrial-scale is investigated. The sulfur content can be reduced from 9000 to less than 10 μg/g at 5.9MPa (H_2 pressure) and 358^{o}C, meeting the requirement of Euro V standard. The Co-Mo-C/mesoporous γ-Al_2O_3 catalyst can even show 5000 h long-term stability. This performance is much better than Co-Mo/mesoporous γ-Al_2O_3 catalyst because the mesoporous γ-Al_2O_3 support with pore diameter of 7.8 could facilitates the removal of large sulfide with diffusion limitation inside the limited pores. In addition, the addition of organic compound leads to

increased acidity and weaker metal-support interaction. This enhances the sulfuration and generates more type II Co-Mo-S active phase. Moreover, the accumulation of coke during the reaction leads to the reduction of pore volume. Nevertheless, the coke be effectively removed by regeneration. The results are of essential reference to the design and development of HDS catalysts.

References

[1] A. A. Asadi, S. M. Alavi, S. J. Royaee, M. Bazmi, Ultra-deep hydrodesulfurization of feedstock containing cracked gasoil through NiMo/γ-Al_2O_3 catalyst pore size optimization, Energy Fuels 32 (2018) 2203-2212.

[2] F. Rashidi, T. Sasaki, A. M. Rashidi, A. N. Kharat, K. J. Jozani, Ultradeep hydrodesulfurization of diesel fuels using highly efficient nanoalumina-supported catalysts: Impact of support, phosphorus, and/or boron on the structure and catalytic activity, J. Catal. 299 (2013) 321-335.

[3] P. A. Nikulshin, A. V. Mozhaev, A. A. Pimerzin, V. V. Konovalov, A. A. Pimerzin, CoMo/Al_2O_3 catalysts prepared on the basis of Co_2Mo_{10}-heteropolyacid and cobalt citrate: Effect of Co/Mo ratio, Fuel 100 (2012) 24-33.

[4] Y. Chen, H. Song, H. Meng, Y. Lu, C. Li, Z. G. Lei, Polyethylene glycol oligomers as green and efficient extractant for extractive catalytic oxidative desulfurization of diesel. Fuel Process. Tech., 158 (2017) 20-25.

[5] J. V. Lauritsen, F. Besenbacher, Atom-resolved scanning tunneling microscopy investigations of molecular adsorption on MoS_2 and CoMoS hydrodesulfurization catalysts, J. Catal. 328 (2015) 49-58.

[6] L. van Haandel, G. Bremmer, E. Hensen, T. Weber, Influence of sulfiding agent and pressure on structure and performance of CoMo/Al_2O_3 hydrodesulfurization catalysts, J. Catal. 342 (2016) 27-39.

[7] Q. Sheng, G. Wang, Y. J. Liu, M. M. Husein, C.D. Gao, Q. Shi, J. S. Gao. Combined Hydrotreating and Fluid Catalytic Cracking Processing for the Conversion of Inferior Coker Gas Oil: Effect on Nitrogen Compounds and Condensed Aromatics. Energy Fuels 32(2018) 4979-4987.

[8] T. Fujikawa, H. Kimura, K. Kiriyama, K. Hagiwara, Development of ultra-deep HDS catalyst for

production of clean diesel fuels, Catal. Today 111 (2006) 188-193.

[9] M.H. Zhang, J.Y. Fan, K. Chi, A. J. Duan, Z. Zhao, X.L. Meng, et al., Synthesis, characterization, and catalytic performance of NiMo catalysts supported on different crystal alumina materials in the hydrodesulfurization of diesel, Fuel Process. Tech. 156 (2017) 446-453.

[10] Y. J. Liu, S. Z. Song, X. Deng, W. Huang, Diesel Ultradeep Hydrodesulfurization over Trimetallic WMoNi Catalysts by a Liquid-Phase Preparation Method in a Slurry Bed Reactor, Energy Fuels 31 (2017) 7372-7381.

[11] T. C. Ho, A theory of ultradeep hydrodesulfurization of diesel in stacked-bed reactors, AIChE J. 64 (2018) 595-605.

[12] W. Chen, X. Long, M. Li, H. Nie, D. Li, Influence of active phase structure of $CoMo/Al_2O_3$ catalyst on the selectivity of hydrodesulfurization and hydrodearomatization, Catal. Today 292 (2017) 97-109.

[13] S. Boonyasuwat, J. Tscheikuna, Co-processing of palm fatty acid distillate and light gas oil in pilot-scale hydrodesulfurization unit over commercial $CoMo/Al_2O_3$, Fuel 199 (2017) 115-124.

[14] O. Klimov, K. Nadeina, Y. V. Vatutina, E. Stolyarova, I. Danilova, E. Y. Gerasimov, et al., $CoMo/Al_2O_3$ hydrotreating catalysts of diesel fuel with improved hydrodenitrogenation activity, Catal. Today 307(2018)73-83.

[15] J. V. Lauritsen, J. Kibsgaard, G. H. Olesen, P. G. Moses, B. Hinnemann, S. Helveg, et al., Location and coordination of promoter atoms in Co-and Ni-promoted MoS_2-based hydrotreating catalysts, J. Catal. 249 (2007) 220-233.

[16] J. Chen, J. Mi, K. Li, X. Wang, E. Dominguez Garcia, Y. Cao, et al., Role of Citric Acid in Preparing Highly Active $CoMo/Al_2O_3$ Catalyst: From Aqueous Impregnation Solution to Active Site Formation, Ind. Eng. Chem. Res. 56 (2017) 14172-14181.

[17] G. M. Dhar, B. Srinivas, M. Rana, M. Kumar, S. Maity, Mixed oxide supported hydrodesulfurization catalysts-a review, Catal. Today 86 (2003) 45-60.

[18] R. Huirache-Acuña, B. Pawelec, E. Rivera-Muñoz, R. Guil-López, J. Fierro, Characterization and HDS activity of sulfided CoMoW/SBA-16 catalysts: Effects of P addition and Mo/(Mo+ W) ratio, Fuel 198 (2017) 145-158.

[19] R. Nava, A. Infantes-Molina, P. Castaño, R. Guil-López, B. Pawelec, Inhibition of CoMo/HMS

catalyst deactivation in the HDS of 4, 6-DMDBT by support modification with phosphate, Fuel 90 (2011) 2726-2737.

[20] S. A. Ali, S. Ahmed, K. W. Ahmed, M. A. Al-Saleh, Simultaneous hydrodesulfurization of dibenzothiophene and substituted dibenzothiophenes over phosphorus modified CoMo/Al_2O= catalysts, Fuel Process. Tech. 98 (2012) 39-44.

[21] X. Feng, J. Yang, X.Z. Duan, Y.Q. Cao, B.X. Chen, W.Y. Chen, D. Lin, G. Qian, D. Chen, C.H. Yang, X.G. Zhou, Enhanced catalytic performance for propene epoxidation with H_2 and O_2 over bimetallic Au-Ag/Uncalcined TS-1 catalysts, ACS Catal. 8 (2018) 7799–7808.

[22] K. S. Triantafyllidis, E. A. Deliyanni, Desulfurization of diesel fuels: Adsorption of 4,6-DMDBT on different origin and surface chemistry nanoporous activated carbons, Chem. Eng. J. 236 (2014) 406-414.

[23] C. Peng, R. Guo, X.C. Fang, Improving ultra-deep desulfurization efficiency by catalyst stacking technology, Catal. Lett. 146 (2016) 701-709.

[24] V. Sundaramurthy, A. Dalai, J. Adjaye, The effect of phosphorus on hydrotreating property of NiMo/γ-Al_2O_3 nitride catalyst, Appl. Catal. A: Gen. 335 (2008) 204-210.

[25] B. Pawelec, J. Fierro, A. Montesinos, T. Zepeda, Influence of the acidity of nanostructured CoMo/P/Ti-HMS catalysts on the HDS of 4, 6-DMDBT reaction pathways, Appl. Catal. B: Environ. 80 (2008) 1-14.

[26] J. D. de León, T. Zepeda, G. Alonso-Nuñez, D. Galván, B. Pawelec, S. Fuentes, Insight of 1D γ-Al_2O_3 nanorods decoration by NiWS nanoslabs in ultra-deep hydrodesulfurization catalyst, J. Catal. 321 (2015) 51-61.

[27] C. Kwak, J. J. Lee, J. S. Bae, S. H. Moon, Poisoning effect of nitrogen compounds on the performance of CoMoS/Al_2O_3 catalyst in the hydrodesulfurization of dibenzothiophene, 4-methyldibenzothiophene, and 4, 6-dimethyldibenzothiophene, Appl. Catal. B: Environ. 35 (2001) 59-68.

[28] X. C. Fang, R. Guo, et al., The development and application of catalysts for ultra-deep hydrodesulfurization of diesel, Chin. J. Catal. 34 (2013) 130-139.

[29] P. Arnoldy, M. Franken, B. Scheffer, J. Moulijn, Temperature-programmed reduction of CoOMo$O_3Al_2O_3$ catalysts, J. Catal. 96 (1985) 381-395.

[30] E. Rodríguez-Castellón, A. Jiménez-López, D. Eliche-Quesada, Nickel and cobalt promoted tungsten and molybdenum sulfide mesoporous catalysts for hydrodesulfurization, Fuel 87 (2008) 1195-1206.

[31] L. Pena, D. Valencia, T. Klimova, CoMo/SBA-15 catalysts prepared with EDTA and citric acid and their performance in hydrodesulfurization of dibenzothiophene, Appl. Catal. B: Environ. 147 (2014) 879-887.

[32] S. Eijsbouts, L. Van den Oetelaar, R. Van Puijenbroek, MoS_2 morphology and promoter segregation in commercial Type 2 Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 hydroprocessing catalysts, J. Catal. 229 (2005) 352-364.

[33] K. Xu, Y. Li, X. Xu, C. Zhou, Z. Liu, F. Yang, et al., Single-walled carbon nanotubes supported Ni-Y as catalyst for ultra-deep hydrodesulfurization of gasoline and diesel, Fuel 160 (2015) 291-296.

[34] F. Rashidi, T. Sasaki, A. M. Rashidi, A. Nemati Kharat, K. J. Jozani, Ultradeep hydrodesulfurization of diesel fuels using highly efficient nanoalumina-supported catalysts: Impact of support, phosphorus, and/or boron on the structure and catalytic activity, J. Catal. 299 (2013) 321-335.

[35] W. Zhou, Q. Zhang, Y. Zhou, Q. Wei, L. Du, S. Ding, et al., Effects of Ga- and P-modified USY-based NiMoS catalysts on ultra-deep hydrodesulfurization for FCC diesels, Catal. Today 305 (2018) 171-181.

[36] S. Shan, H. Liu, Y. Yue, G. Shi, X. Bao, Trimetallic WMoNi diesel ultra-deep hydrodesulfurization catalysts with enhanced synergism prepared from inorganic–organic hybrid nanocrystals, J. Catal. 344 (2016) 325-333.

[37] L. Peña, D. Valencia, T. Klimova, CoMo/SBA-15 catalysts prepared with EDTA and citric acid and their performance in hydrodesulfurization of dibenzothiophene, Appl. Catal. B: Environ. 147 (2014) 879-887.

[38] T. Kabe, W. H. Qian, S. Ogawa, A. Ishihara, Mechanism of Hydrodesulfurization of Dibenzothiophene on Co-Mo/Al_2O_3 and Co/Al_2O_3 Catalyst by the Use of Radioisotope 35S Tracer, J. Catal.143 (1993) 239-248.

Table Captions:

Table 1 Acidity for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Table 2 HRTEM statistic results of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Table 3 XPS results of sulfurized Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.

Table 4 Properties of testing feedstocks for HDS reaction.

Table 5 Comparison of HDS results for different catalysts.

Table 6 Comparing the catalytic activity of the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst and other reported catalysts.

Table 7 Reaction conditions and results in hydrotreating unit.

Table 1 Acidity for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Catalysts	Total acidity (μmol/g)	Brönsted (μmol/g)	Lewis (μmol/g)	B/L ratio
Co-Mo-C/mesoporous γ-Al_2O_3	544	139	405	0.34
Co-Mo/mesoporous γ-Al_2O_3	487	44	443	0.10

Table 2 HRTEM statistic results of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Properties	Co-Mo/mesoporous γ-Al_2O_3	Co-Mo-C/mesoporous γ-Al_2O_3
Maximum slab length (nm)	17.3	11.1
Average slab length (nm)	9.5	4.8
Percentage of 1-2 layers	75.2	47.9
Percentage of 3-5 layers	20.1	49.7
Percentage of >5 layers	4.7	2.4

Table 3 XPS results of sulfurized Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.

Catalyst	Co-Mo/mesoporous γ-Al_2O_3	Co-Mo-C/mesoporous γ-Al_2O_3
$Mo^{4+}/(Mo^{4+}+Mo^{5+}+Mo^{6+})$ (%)	65.88	75.03
S/Mo	1.74	1.78
Mo $3d_{5/2}$ BE (eV)	228.8	228.5
Co $2p_{3/2}$ BE (eV)	780.1	778.4

Table 4 Properties of testing feedstocks for HDS reaction.

Feedstock	Diesel oil
Density at 20°C (g/cm^3)	0.8397
Distillation range (°C)	
IBP (10%)	151/189
30%/50%	242/286
70%/90%	312/352
95%/FBP	366/378
Sulfur content (μg·g^{-1})	9000
Nitrogen content (μg·g^{-1})	150
4,6-DMDBT content (μg·g^{-1})	192

Table 5 Comparison of HDS results for different catalysts.

Feedstock	Diesel oil			
Catalyst	Co-Mo-C/mesoporous γ-Al_2O_3		Co-Mo/mesoporous γ-Al_2O_3	
HDS conditions				
Average reaction temperature (^oC)	360	370	360	370
Hydrogen pressure (MPa)	6.0	6.0	6.0	6.0
Space velocity (h^{-1})	0.77	0.77	0.77	0.77
Hydrogen/oil ratio	400	400	400	400
Sulfur content ($\mu g \cdot g^{-1}$)	7.4	4.0	12.0	7.0
Nitrogen content ($\mu g \cdot g^{-1}$)	2.4	2.2	5.0	4.0
4,6-DMDBT content ($\mu g \cdot g^{-1}$)	4.2	2.5	8.2	4.6

Table 6 Comparing the catalytic activity of the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst and other reported catalysts.

Catalysts	Sulfur Concentration (ppm)	Conversion (%)	Temperature(^oC)	Stability (h)	Reference
Co-Mo-C/mesoporous γ-Al_2O_3	9000	99.9	358	5000	This work
CoMoPB/nanoAl_2O_3	13500	99.9	350	-	[34]
PGaHUSY	2259	99.7	360	-	[38]
WMoNi-HHD	3904	99.5	360	500	[37]
WMoNi/Al_2O_3	-	96.0	360	-	[10]
CoMo/SBA-15	2160	77	3000	-	[36]
Co-Mo/Al_2O_3	4000	67	3000	-	[35]

Table 7 Reaction conditions and results in hydrotreating unit.

Catalyst	Co-Mo-C/mesoporous γ-Al_2O_3	
Diesel	Feedstock	Product
Density at 20^oC (g/m^3)	839.0	831.6
Distillation range (D86, ^oC)		
IBP/10%	158/191	175/198
30%/50%	233/275	232/274
70%/90	313/349	311/348
95%/FBP	363/367	362/365
Sulfur content ($\mu g \cdot g^{-1}$)	9000	7.8

Figure Captions:

Fig. 1 Schematic process flow diagram of 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization.

Fig. 2 XRD patterns (a) of mesoporous γ-Al_2O_3 support and N_2 physisorption (b) of catalysts.

Fig. 3 H_2-TPR spectra of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Fig. 4 Typical HRTEM of Co-Mo/mesoporous γ-Al_2O_3 (a) and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts (b).

Fig. 5 Industrial-scale 3000 kt/a stability evaluation (a) in a hydrotreating plant (b).

Fig. 6 N_2 adsorption-desorption isotherms of fresh, deactivated and regenerated Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.

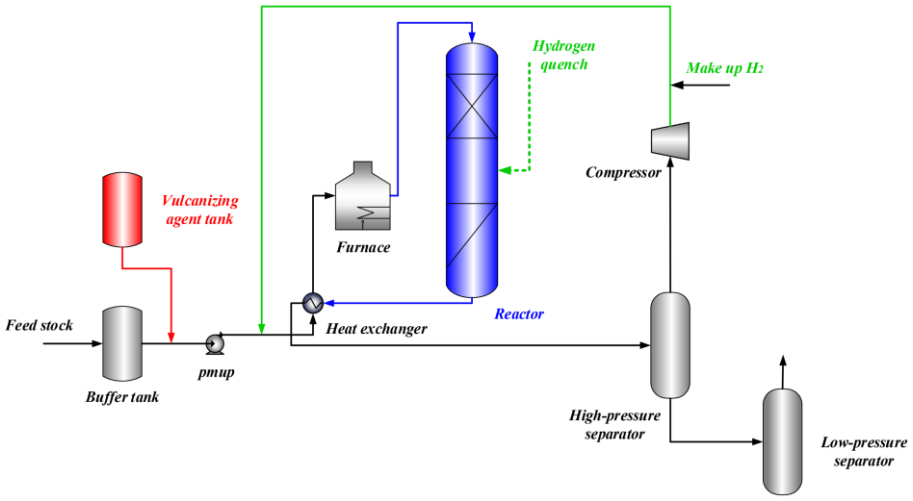

Fig. 1 Schematic process flow diagram of 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization.

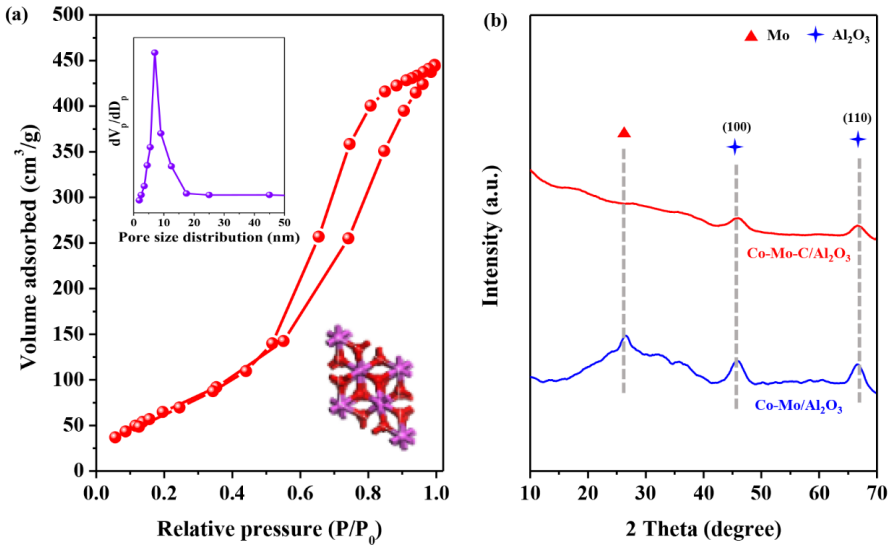

Fig. 2 XRD patterns (a) of mesoporous γ-Al_2O_3 support and N_2 physisorption (b) of catalysts.

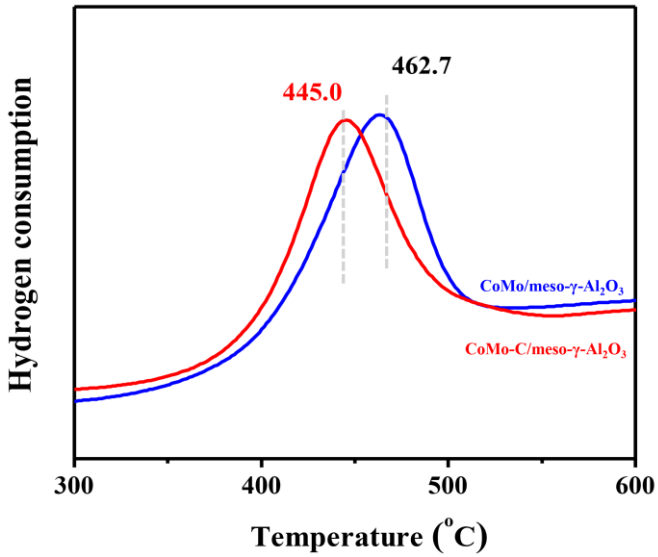

Fig. 3 H_2-TPR spectra of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

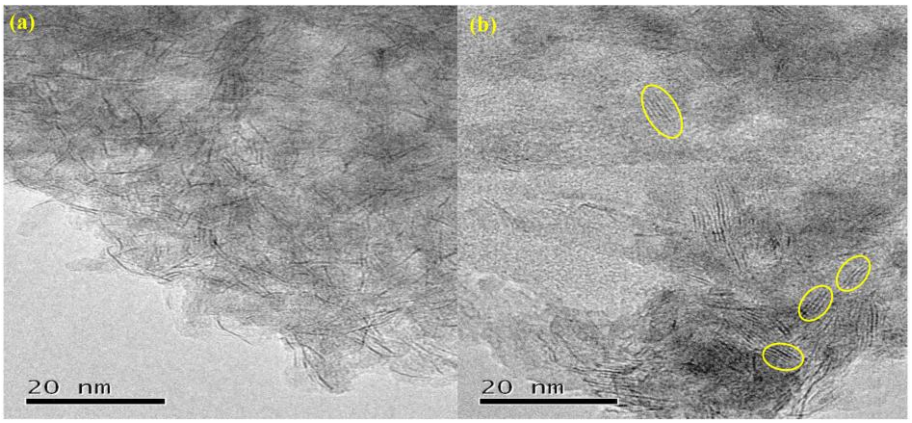

Fig. 4 Typical HRTEM of Co-Mo/mesoporous γ-Al_2O_3 (a) and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts (b).

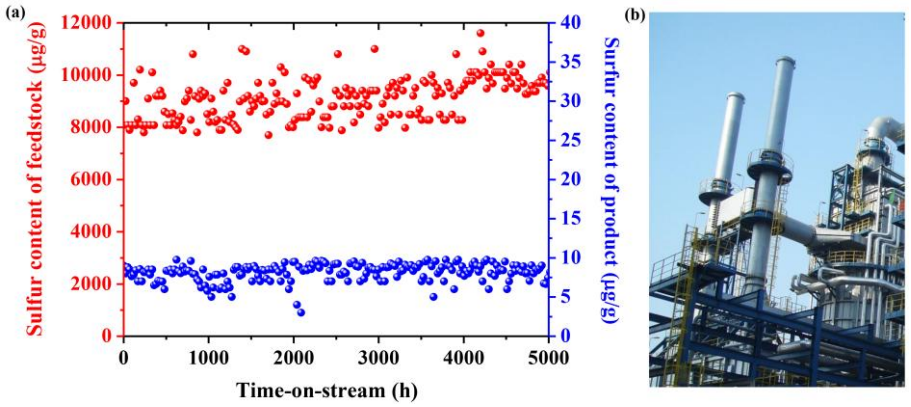

Fig. 5 Industrial-scale 3000 kt/a stability evaluation (a) in a hydrotreating plant (b).

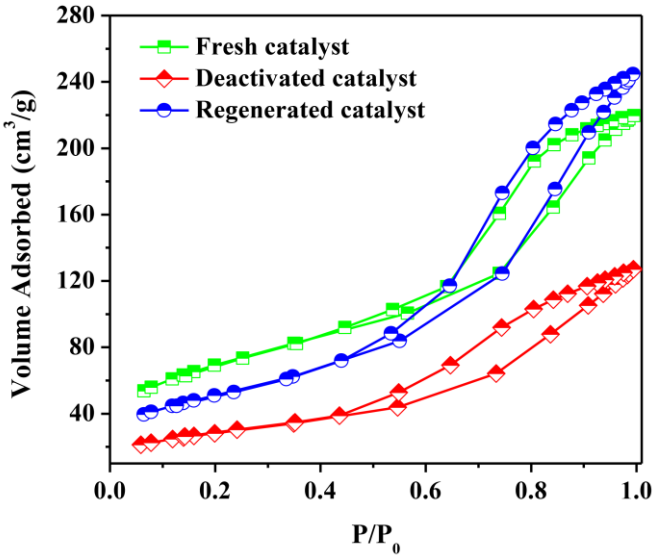

Fig. 6 N_2 adsorption-desorption isotherms of fresh, deactivated and regenerated Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.

Tailoring the structure of Co-Mo/mesoporous γ-Al_2O_3 catalysts by adding multi-hydroxyl compound: A 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization study

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Abstract: Ever-increasing concern on environmental impacts (e.g., sulfur pollution) by fossil fuels has triggered the research on hydrodesulfurization (HDS). In this work, Co-Mo nanoparticles were deposited on the mesoporous γ-Al_2O_3 support with the addition of organic compound, and the physico-chemical properties of the catalysts (Co-Mo-C/mesoporous γ-Al_2O_3) were then characterized by multi-techniques such as H_2-TPR, HRTEM, XPS, N_2 physisorption. It is found that the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is easier to be reduced when organic compound is added, enhancing the sulfuration. This results in better dispersion of Co-Mo-S species and more Co-Mo-S II active sites, which significantly enhance diesel ultra-deep hydrodesulfurization activity. Furthermore, this novel catalyst was also tested for HDS reaction in a 3000 kt/a industrial-scale plant. Gratifyingly, this catalyst showed effective reduction of sulfur content from 9000 to less than 10 μg/g and also high stability over 5000 h. The results are of great significance to the design and development of industrial HDS catalysts.

Keywords: hydrodesulfurization; diesel; structure manipulation; Co-Mo/mesoporous Al_2O_3; industrial-scale

1. Introduction

Growing concern on environment necessitates the elimination of heteroatoms such as sulfur and nitrogen from fossil fuels. This worldwide demand for clean fuels leads to strict legislation to control and decrease the environmental impacts of fossil fuels on the environment and human beings. For example, Euro V standard of diesel fuel strictly requires that the diesel sulfur content is less than 10 ppm[1]. However, the removal of refractive sulfur-containing alkyl derivatives of dibenzothiophene (DBTs)[2], such as 4-dimethyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), is quite challenging. Ultra-deep hydrodesulfurization (HDS) to produce ultra-low-sulfur[3] diesel fuels with sulfur content of less than 10 ppm is one of the most essential industrial processes to resolve the above problem[4-6]. This has triggered the great attention of researchers on developing highly efficient catalysts for HDS [7-11].

The most important HDS catalyst used in oil refineries is usually the Co(Ni)Mo/Al_2O_3 catalysts [12-14]. The structure of the typical Co(Ni)-Mo catalyst can be briefly described by the Co(Ni)-Mo-S model, which was first reported by Topsøe[15] The structure of catalytically active Co(Ni)-Mo-S sites is formed by the decoration of Co(Ni) atoms on the well-dispersed MoS_2 nanocrystals[16]. These active sites can be obtained by the sulfidation process[3]. It is widely accepted that the HDS activity and stability of the catalysts are greatly affected by the physico-chemical properties of the support and metals [1, 2]. Al_2O_3 in α and γ forms is the most common support for HDS catalysts because of its outstanding textural and mechanical properties. Normally, these properties can be easily tuned based on the detailed reaction requirements, feedstock compositions and product's targeted specifications[17].

Besides the properties of support, the interaction between the support and Co-Mo metals are usually quite essential to the design of effective HDS catalyst. It was reported that using chelating agents or additives such as P and B can reduce the interaction between active metals and aluminum supports, producing more active HDS sites [18-20]. Although much attention has been devoted to understanding the effect of support properties on HDS performance, few reports were focused on enhancing catalytic performance by manipulating the metal-support interaction aiming at industrial application. There is urgent need to design suitable catalyst for industrial HDS reaction, which is of prime scientific and industrial importance.

In this work, the effects of organic compound on catalyst structure and HDS performance are investigated, aiming at the industrial-scale HDS process development. Mesoporous γ-Al_2O_3 is first employed as support, and then load Co-Mo nanoparticles with the addition of organic compound. The physico-chemical properties of the catalysts are studied by multi-techniques such as XRD, XPS, TPR, HRTEM, NH_3-TPD and Py-IR. It is found that the introduction of organic compound makes the catalyst easily reduced, generating more type II Co-Mo-S active sites and enhancing the HDS activity and stability. Moreover, this catalyst is also tested in an 3000 kt/a industrial-scale HDS unit, and shows fantastic 99.9% sulfur reduction from 9000 to less than 10 μg/g over 5000 h. The properties of the used catalyst after long-term evaluation and regeneration are further discussed. The results reported herein are of great referential importance to the design of industrial catalysts, and is expected to be extended to other HDS catalysts.

2. Experimental

2.1 Synthesis of Co-Mo/mesoporous γ-Al_2O_3 catalyst

The mesoporous γ-Al_2O_3 support was provided by Fushun Catalysts Factory of

SINOPEC. Two Co-Mo catalysts were prepared by impregnation with an aqueous solution of cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$] and ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] with and without the addition of multi-hydroxyl compound. The loadings of Mo and Co oxides are 18 and 3wt%, respectively. The resultant catalysts were then dried at 110 ^oC and calcined at 500 ^oC for 3 h. The catalysts were then subjected to sulfidation. Typically, the catalyst was placed in a reactor at 4 MPa of H_2 and heated to 110 ^oC. Sulfidizing oil (96% kerosene and 4% CS_2) was then added into the reactor and maintained for 3 h. Afterwards, the reactor was heated to 360 ^oC for 8 h. The resultant catalyst prepared with the addition of multi-hydroxyl compound is named as Co-Mo-C/mesoporous γ-Al_2O_3. For comparison, the catalyst without multi-hydroxyl compound addition is denoted as Co-Mo/mesoporous γ-Al_2O_3.

2.2 Characterizations

N_2 physisorption was performed on a Micromeritics ASAP 2020 instrument at -196 ^oC. Each sample was heated to 300 ^oC under vacuum for 3 h prior to testing. The XRD patterns of the catalysts were determined on a Rigaku Miniflex powder diffractometer with CuK_α radiation (λ=0.154 nm). TPR curves were obtained on a Micromeritics AutoChem 2920 instrument to analyze the reducibility of the catalysts. All samples were calcined at 450 ^oC for 1 h and then heated from room temperature to 1000^oC in a 10% H_2/Ar mixture. XPS were performed on a Multilab2000X instrument (ThermoFisher) using Mg-K_α radiation. All spectra were corrected using 284.6 eV as the reference for C1s binding energy. HRTEM measurements were conducted on a JEM-2100 instrument operating at 200 kV. The sulfur content was obtained by sulfur content analysis (ANTEK-9000) using Ar and O_2 as carrier and burning gas, respectively. The analysis standard was SH/T0689-2000. NH_3-TPD was conducted as follows: the catalysts after calcination were saturated with NH_3 for 30 min at 100^oC. Afterwards, He

was flushed to remove the physically adsorbed molecules. The TPD results were collected in He from 323 to 873 K with a heating rate of 10 K/min. Py-adsorbed IR spectra were recorded on a PE FTIR Frontier instrument. The system was degassed at 500 ^{o}C for 5 h under vacuum and flushed by pure pyridine at room temperature for 20 min. The infrared (IR) spectra were then recorded.

2.3 Catalytic testing in a 3000 kt/a industrial unit

The industrial-scale HDS reaction was carried out in a fixed bed reactor, and the corresponding schematic diagram is illustrated in Fig. 1. Typically, Co-Mo-C/mesoporous γ-Al_2O_3 catalyst was shaped into particle with size of 1-3 mm. Both the top and bottom of the fixed bed reactor were filled with inert particles. The catalysts were loaded into reactor of D/d_p > 18, L/d_p >350, where D, L and d_p are the inner diameter, height of bed and catalysis particle size, respectively. The feedstock was pumped into the furnace, and was heated first through heat exchanger. The heated feedstock was then introduced into the reactor. After reaction, the final products were separated by high-pressure and low-pressure separators.

(Figure 1 should be inserted herein)

3. Results and discussions

3.1 Effect of organic compound on catalyst structure

The mesoporous γ-Al_2O_3 support in this work was first characterized by N_2 physisorption, as shown in Fig. 2a. According to the IUPAC classification, it can be seen that this support has Type IV adsorption-desorption isotherms[1, 21], revealing the mesoporous characteristic. The hysteresis loop of the isotherm starts at ~0.4, indicating that the mesopores are intracrystalline rather than intercrystalline. From the inset of Fig.

2a, it is observed that the mesoporous γ-Al_2O_3 support has average pore size (ca. 7.8 nm). The detailed information of pore structure is summarized in Table S1. The pore volume and surface area of mesoporous γ-Al_2O_3 support are normally larger than those of a typical commercial Al_2O_3 support. Among the structural and textural properties, pore size is extremely essential because the diffusion of different species inside pores of Al_2O_3 could affect and limit the HDS overall reaction rate. It is reported that the size of 4,6-DMDBT molecules estimated by molecular orbital calculations is 0.59 × 0.89 nm[22]. This pore size is favorable for the diffusion of the sulfur-containing alkyl derivatives of dibenzothiophene. Based on this mesoporous γ-Al_2O_3 support, Co-Mo nanoparticles are deposited on support with the addition of the compound. To better show the role of the compound, Co-Mo/mesoporous γ-Al_2O_3 catalyst without the addition of compound is compared. Fig. 2b shows the XRD patterns of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst. Both of the two samples exhibit intense peaks at 46^o and 66.8^o, which are correlated to the planes (100) and (110) of the γ-Al_2O_3 phase (JCPDF#29-0063)[23], respectively. There is no low-intensity broad peaks between 16^o and 32^o, indicating the absence of amorphous Al_2O_3 phase. For Co-Mo/mesoporous γ-Al_2O_3 catalyst, there is a peak at 26^o which is related to the MoO_3 (021) species. In comparison, no peak shows up at 26^o for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst, indicating that the particles are well-dispersed on support.

(Figure 2 should be inserted herein)

Acidity of a catalyst is a key parameter affecting the HDS performance[24]. For the mesoporous γ-Al_2O_3 support, there are three kinds of NH_3-TPD peaks corresponding to different strengths, i.e., weak acidity (150-250^{o}C), medium acidity (250-450^{o}C) and strong acidity (>450^{o}C) [25, 26]. The total acid content includes 36.0% weak acidity,

64.0% medium acidity and 0% strong acidity. The total acid content of mesoporous γ-Al_2O_3 support is 0.654 mmol/g. After loading CoMo nanoparticles, the Lewis and Brönsted sites of the two catalysts are determined by Py-IR. The bands at 1445 and 1556 cm^{-1} are attributed to the pyridine chemisorbed on Lewis sites and the vibration mode of pyridinium ion adsorbed on Brönsted sites, respectively[27]. In addition, the pyridine adsorbed on both Lewis and Brønsted sites show up at 1486 cm^{-1}. The numbers of sites and B/L ratio of the two catalysts are listed in Table 1. It can be seen from Table 1 that total acid sites together with B/L ratio are all larger on Co-Mo-C/mesoporous γ-Al_2O_3 than those on Co-Mo/mesoporous γ-Al_2O_3 catalyst, possibly due to the formation of complex between metal and multi-hydroxyl compound. This could greatly affect the HDS reaction. It is reported that higher total acidity with larger B/L ratio could enhance the HDS performance [28]. Therefore, the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is expected to show better HDS activity.

(Table 1 should be inserted herein)

The interaction between metal and support is then investigated by H_2-TPR, which is a powerful technique to investigate the reduction behavior of supported phases. Fig. 3 shows the H_2-TPR spectra of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts. According to Moulijn et al.[29], there is a reduction peak of well-dispersed molybdenum supported species at low temperature of ca. 450^oC. This is attributed to the partial reduction of Mo(VI) to Mo(IV) of amorphous, highly defective, multilayered oxides (octahedral Mo species) bounded to Al_2O_3 support[30, 31]. It is clear that the intense peak for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is located at 445^oC, which is lower than 462.7^oC for Co-Mo/mesoporous γ-Al_2O_3 catalyst, demonstrating that the interaction between metal and support is weak for Co-Mo-

C/mesoporous γ-Al_2O_3 catalyst. This weak interaction is reported to be beneficial to the catalytic performance of HDS reaction due to the formation of Co-Mo-S type II sites[2]. Moreover, the absence of additional reduction peaks at 350 ◦C indicate that Co oxide supported crystallites is not formed on the supports.

(Figure 3 should be inserted herein)

To obtain information regarding the morphology and distribution of Co-Mo-S crystallites, the two catalysts are then analyzed by HRTEM, and the typical HRTEM images are shown in Fig. 4. Due to the good dispersion of Co, the Co nanoparticles can not be observed by HRTEM characterization[32]. This is also in accordance with the XRD results in Fig. 2b. The black thread-like fringes are the Co-Mo-S phase. The average Co-Mo-S slab length (L) can be calculated from the following equation (3-1):

$$\bar{L} = \frac{\sum_{i=1}^{n} n_i l_i}{\sum_{i=1}^{n} n_i} \quad (3\text{-}1)$$

where l_i is the length of *i*th slab, n_i is the number of particle with a l_i length. The statistical results of the length and stacking distributions of Co-Mo-S for the two catalysts are shown in Table 2. Maximum slab length of Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is smaller, and the average length of the slabs on Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is 4.8 nm, shorter than the 9.5 nm for Co-Mo/mesoporous γ-Al_2O_3 catalyst. In addition, the percentages of Co-Mo-S slabs with 1-2 layers are 75.2 and 47.9% for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts, respectively. The percentages of 3-5 layers of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are 20.1 and 49.7%, respectively. The results show that the addition of compound decrease the interaction between metal and support. Therefore,

the average length reduces and the dispersion increases. Moreover, it is reported that the phase with 3-5 layers is Co-Mo-S type II, which could exhibit superior HDS performance than Co-Mo-S type I (1-2 layers)[33].

(Figure 4 should be inserted herein)

(Table 2 should be inserted herein)

The surface concentrations of Mo in multiple oxidation states, and the binding energies of Co and Mo can be determined by XPS, as shown in Table 3. The catalysts are stored in nitrogen before XPS test to prevent the re-oxidation by air. The typical curve-fitting of Mo 3d is shown in Fig. S1. The Mo 3d spectra can be divided into three sets of doublets, which correspond to the Mo^{4+}, Mo^{5+} and Mo^{6+} species[2]. The Mo^{4+} species is usually MoS_2, which is usually regarded as the active phase[28]. The Mo^{5+} and Mo^{6+} species can be attributed to Mo oxy-sulfide and not completely sulfided Mo species, respectively. From Fig. S1 and Table 3, it is seen that the percentage of Mo^{4+} in the sum of Mo^{4+}, Mo^{5+} and Mo^{6+} species is 75.03% for Co-Mo-C/mesoporous γ-Al_2O_3. In comparison, this value for Co-Mo/mesoporous γ-Al_2O_3 catalyst is only 65.88%. In addition, it is also noticed that the Mo binding energy for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is also lower than that for Co-Mo/mesoporous γ-Al_2O_3 catalyst. The lower binding energy and higher percentage of Mo^{4+} all suggest that the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst has weaker interaction between metal and support, and thus is more easily sulfided, leading to more Co-Mo-S active phases. This finding is also in accordance with the finding of H_2-TPR (Fig. 3) and HRTEM (Fig. 4) results.

(Table 3 should be inserted herein)

3.2 Catalytic performance of Co-Mo-C/mesoporous Al_2O_3 catalyst

The Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are then tested for HDS reaction. The properties of the testing diesel oil are shown in Table 4. The sulfur content for this diesel oil is 9000 $\mu g \cdot g^{-1}$. From table 4, it is seen the diesel has high sulfur and low nitrogen content, high 95% and FBP, indicating the difficulty of HDS. The HDS results at different temperature for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are summarized in Table 5. At 360^oC, 6.0 MPa (H_2 pressure) and 0.77 h^{-1}, Co-Mo/mesoporous γ-Al_2O_3 catalyst shows poor HDS performance with the product sulfur content of 12 $\mu g \cdot g^{-1}$. In contrast, the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst has better performance. The low sulfur content of 7.4 $\mu g \cdot g^{-1}$ meets the requirement of Euro V standard. Further increasing the reaction temperature leads to reduced sulfur contents. The values for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts are 7.0 and 4.0 $\mu g \cdot g^{-1}$, respectively. Therefore, the temperature for Co-Mo-C/mesoporous γ-Al_2O_3 catalyst could be 10^oC lower than that for Co-Mo/mesoporous γ-Al_2O_3 catalyst, which could greatly reduce the energy consumption.

(Table 4 should be inserted herein)

(Table 5 should be inserted herein)

From the above results, the main reasons for the enhanced performance for Co-Mo-C/mesoporous γ-Al_2O_3 support could be the more active Co-Mo-S type II species, which are originated from weak interaction between metal and support. The higher activity of Co-Mo-S Type II is generally associated to the high staking number of slabs bonding weakly to the support through a small Mo-O-Al linkage[34]. Moreover, it is also reported that the normal HDS reaction routes[28] include hydrogenation, direct hydrogenolysis and alkyl transfer desulfurization. Higher B/L ratio and presence of Co-Mo-S type II species may also lead to better alkyl transfer desulfurization of refractory

sulfides such as 4, 6-DMDBT[23, 28]. The ultradeep hydrodesulfurization performance of Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is compared with reported catalysts. It can be seen in Table 6 that the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst shows a high activity compared to catalysts reported in the literature[10, 34-38].

(Table 6 should be inserted herein)

It has been confirmed that Co-Mo-C/mesoporous γ-Al_2O_3 catalyst has enhanced performance for HDS reaction. To further verify the stability of this catalyst, the long-term stability is subsequently evaluated in industrial-scale 3000kt/a plant. The reaction conditions and results are shown in Table 7 and Fig. 5. The HDS reaction works at low H_2 pressure P=5.9 MPa, inlet temperature T_i=350^{o}C, outlet temperature T_o=362^{o}C, average temperature T_a=358^{o}C, hydrogen to oil ratio=308 and space velocity V=0.70h^{-1}. Clearly, the industrial evaluation of Co-Mo-C/mesoporous γ-Al_2O_3 catalyst also meets the Euro V requirement of diesel with low sulfur content of 7.8 μg·g^{-1}. The long-term evaluation of catalyst at the same reaction condition is shown in Fig. 5. The catalyst maintains high stability with the low product sulfur content (i.e., smaller than 10 μg·g^{-1}) over 5000 h. The reason for the good catalytic stability should be the enhanced mass transfer ability together with the unique structure of active Co-Mo-S sites.

(Table 7 should be inserted herein)

(Figure 5 should be inserted herein)

It should be noted that the coke formation on Co-Mo-C/mesoporous γ-Al_2O_3 catalyst is inevitable due to the contact with carbonaceous feedstock during the long-term stability test. Therefore, the reaction temperature is normally increased by ca. 0.5^{o}C/month to maintain the quality of products. After long running time, the catalyst

should be regenerated. The fresh, used and regenerated catalysts in air at 420^{o}C are then characterized by N_2 physisorption. Fig. 6 shows that all of the three samples show similar type IV adsorption-desorption isotherms. The hysteresis loop of the isotherm for the samples all start at ca. 0.4, indicating that the mesoporous structure is well maintained. The pore volume of the fresh catalyst is 0.33 cm^3/g, which decreases to 0.19 cm^3/g after long-term testing. The regeneration successfully removes the carbonaceous deposits inside the pores, and increases the pore volume from 0.19 cm^3/g to 0.33 cm^3/g, which is almost the same to fresh catalyst. By using this catalyst, the 3000 kt/a industrial plant in China with the catalyst technique from SINOPEC has been running smoothly for 3 years. After 3 years, the regenerated catalyst also shows good HDS performance (Table S2-3). This Co-Mo-C/mesoporous γ-Al_2O_3 catalyst shows good performance with the reduced reaction temperature, saving the energy consumption and greatly increasing the profit. This catalyst is also of referential importance to the design of industrial catalyst for diesel ultra-deep hydrodesulfurization.

(Figure 6 should be inserted herein)

4. Conclusion

In this work, hydrodesulfurization reaction catalyzed by Co-Mo-C/mesoporous γ-Al_2O_3 catalyst at 3000 kt/a industrial-scale is investigated. The sulfur content can be reduced from 9000 to less than 10 μg/g at 5.9MPa (H_2 pressure) and 358^{o}C, meeting the requirement of Euro V standard. The Co-Mo-C/mesoporous γ-Al_2O_3 catalyst can even show 5000 h long-term stability. This performance is much better than Co-Mo/mesoporous γ-Al_2O_3 catalyst because the mesoporous γ-Al_2O_3 support with pore diameter of 7.8 could facilitates the removal of large sulfide with diffusion limitation inside the limited pores. In addition, the addition of organic compound leads to

increased acidity and weaker metal-support interaction. This enhances the sulfuration and generates more type II Co-Mo-S active phase. Moreover, the accumulation of coke during the reaction leads to the reduction of pore volume. Nevertheless, the coke be effectively removed by regeneration. The results are of essential reference to the design and development of HDS catalysts.

References

[1] A. A. Asadi, S. M. Alavi, S. J. Royaee, M. Bazmi, Ultra-deep hydrodesulfurization of feedstock containing cracked gasoil through NiMo/γ-Al_2O_3 catalyst pore size optimization, Energy Fuels 32 (2018) 2203-2212.

[2] F. Rashidi, T. Sasaki, A. M. Rashidi, A. N. Kharat, K. J. Jozani, Ultradeep hydrodesulfurization of diesel fuels using highly efficient nanoalumina-supported catalysts: Impact of support, phosphorus, and/or boron on the structure and catalytic activity, J. Catal. 299 (2013) 321-335.

[3] P. A. Nikulshin, A. V. Mozhaev, A. A. Pimerzin, V. V. Konovalov, A. A. Pimerzin, CoMo/Al_2O_3 catalysts prepared on the basis of Co_2Mo_{10}-heteropolyacid and cobalt citrate: Effect of Co/Mo ratio, Fuel 100 (2012) 24-33.

[4] Y. Chen, H. Song, H. Meng, Y. Lu, C. Li, Z. G. Lei, Polyethylene glycol oligomers as green and efficient extractant for extractive catalytic oxidative desulfurization of diesel. Fuel Process. Tech., 158 (2017) 20-25.

[5] J. V. Lauritsen, F. Besenbacher, Atom-resolved scanning tunneling microscopy investigations of molecular adsorption on MoS_2 and CoMoS hydrodesulfurization catalysts, J. Catal. 328 (2015) 49-58.

[6] L. van Haandel, G. Bremmer, E. Hensen, T. Weber, Influence of sulfiding agent and pressure on structure and performance of CoMo/Al_2O_3 hydrodesulfurization catalysts, J. Catal. 342 (2016) 27-39.

[7] Q. Sheng, G. Wang, Y. J. Liu, M. M. Husein, C.D. Gao, Q. Shi, J. S. Gao. Combined Hydrotreating and Fluid Catalytic Cracking Processing for the Conversion of Inferior Coker Gas Oil: Effect on Nitrogen Compounds and Condensed Aromatics. Energy Fuels 32(2018) 4979-4987.

[8] T. Fujikawa, H. Kimura, K. Kiriyama, K. Hagiwara, Development of ultra-deep HDS catalyst for

production of clean diesel fuels, Catal. Today 111 (2006) 188-193.

[9] M.H. Zhang, J.Y. Fan, K. Chi, A. J. Duan, Z. Zhao, X.L. Meng, et al., Synthesis, characterization, and catalytic performance of NiMo catalysts supported on different crystal alumina materials in the hydrodesulfurization of diesel, Fuel Process. Tech. 156 (2017) 446-453.

[10] Y. J. Liu, S. Z. Song, X. Deng, W. Huang, Diesel Ultradeep Hydrodesulfurization over Trimetallic WMoNi Catalysts by a Liquid-Phase Preparation Method in a Slurry Bed Reactor, Energy Fuels 31 (2017) 7372-7381.

[11] T. C. Ho, A theory of ultradeep hydrodesulfurization of diesel in stacked-bed reactors, AIChE J. 64 (2018) 595-605.

[12] W. Chen, X. Long, M. Li, H. Nie, D. Li, Influence of active phase structure of $CoMo/Al_2O_3$ catalyst on the selectivity of hydrodesulfurization and hydrodearomatization, Catal. Today 292 (2017) 97-109.

[13] S. Boonyasuwat, J. Tscheikuna, Co-processing of palm fatty acid distillate and light gas oil in pilot-scale hydrodesulfurization unit over commercial $CoMo/Al_2O_3$, Fuel 199 (2017) 115-124.

[14] O. Klimov, K. Nadeina, Y. V. Vatutina, E. Stolyarova, I. Danilova, E. Y. Gerasimov, et al., $CoMo/Al_2O_3$ hydrotreating catalysts of diesel fuel with improved hydrodenitrogenation activity, Catal. Today 307(2018)73-83.

[15] J. V. Lauritsen, J. Kibsgaard, G. H. Olesen, P. G. Moses, B. Hinnemann, S. Helveg, et al., Location and coordination of promoter atoms in Co-and Ni-promoted MoS_2-based hydrotreating catalysts, J. Catal. 249 (2007) 220-233.

[16] J. Chen, J. Mi, K. Li, X. Wang, E. Dominguez Garcia, Y. Cao, et al., Role of Citric Acid in Preparing Highly Active $CoMo/Al_2O_3$ Catalyst: From Aqueous Impregnation Solution to Active Site Formation, Ind. Eng. Chem. Res. 56 (2017) 14172-14181.

[17] G. M. Dhar, B. Srinivas, M. Rana, M. Kumar, S. Maity, Mixed oxide supported hydrodesulfurization catalysts-a review, Catal. Today 86 (2003) 45-60.

[18] R. Huirache-Acuña, B. Pawelec, E. Rivera-Muñoz, R. Guil-López, J. Fierro, Characterization and HDS activity of sulfided CoMoW/SBA-16 catalysts: Effects of P addition and Mo/(Mo+ W) ratio, Fuel 198 (2017) 145-158.

[19] R. Nava, A. Infantes-Molina, P. Castaño, R. Guil-López, B. Pawelec, Inhibition of CoMo/HMS

catalyst deactivation in the HDS of 4, 6-DMDBT by support modification with phosphate, Fuel 90 (2011) 2726-2737.

[20] S. A. Ali, S. Ahmed, K. W. Ahmed, M. A. Al-Saleh, Simultaneous hydrodesulfurization of dibenzothiophene and substituted dibenzothiophenes over phosphorus modified CoMo/Al_2O= catalysts, Fuel Process. Tech. 98 (2012) 39-44.

[21] X. Feng, J. Yang, X.Z. Duan, Y.Q. Cao, B.X. Chen, W.Y. Chen, D. Lin, G. Qian, D. Chen, C.H. Yang, X.G. Zhou, Enhanced catalytic performance for propene epoxidation with H_2 and O_2 over bimetallic Au-Ag/Uncalcined TS-1 catalysts, ACS Catal. 8 (2018) 7799–7808.

[22] K. S. Triantafyllidis, E. A. Deliyanni, Desulfurization of diesel fuels: Adsorption of 4,6-DMDBT on different origin and surface chemistry nanoporous activated carbons, Chem. Eng. J. 236 (2014) 406-414.

[23] C. Peng, R. Guo, X.C. Fang, Improving ultra-deep desulfurization efficiency by catalyst stacking technology, Catal. Lett. 146 (2016) 701-709.

[24] V. Sundaramurthy, A. Dalai, J. Adjaye, The effect of phosphorus on hydrotreating property of NiMo/γ-Al_2O_3 nitride catalyst, Appl. Catal. A: Gen. 335 (2008) 204-210.

[25] B. Pawelec, J. Fierro, A. Montesinos, T. Zepeda, Influence of the acidity of nanostructured CoMo/P/Ti-HMS catalysts on the HDS of 4, 6-DMDBT reaction pathways, Appl. Catal. B: Environ. 80 (2008) 1-14.

[26] J. D. de León, T. Zepeda, G. Alonso-Nuñez, D. Galván, B. Pawelec, S. Fuentes, Insight of 1D γ-Al_2O_3 nanorods decoration by NiWS nanoslabs in ultra-deep hydrodesulfurization catalyst, J. Catal. 321 (2015) 51-61.

[27] C. Kwak, J. J. Lee, J. S. Bae, S. H. Moon, Poisoning effect of nitrogen compounds on the performance of CoMoS/Al_2O_3 catalyst in the hydrodesulfurization of dibenzothiophene, 4-methyldibenzothiophene, and 4, 6-dimethyldibenzothiophene, Appl. Catal. B: Environ. 35 (2001) 59-68.

[28] X. C. Fang, R. Guo, et al., The development and application of catalysts for ultra-deep hydrodesulfurization of diesel, Chin. J. Catal. 34 (2013) 130-139.

[29] P. Arnoldy, M. Franken, B. Scheffer, J. Moulijn, Temperature-programmed reduction of $CoOMoO_3Al_2O_3$ catalysts, J. Catal. 96 (1985) 381-395.

[30] E. Rodríguez-Castellón, A. Jiménez-López, D. Eliche-Quesada, Nickel and cobalt promoted tungsten and molybdenum sulfide mesoporous catalysts for hydrodesulfurization, Fuel 87 (2008) 1195-1206.

[31] L. Pena, D. Valencia, T. Klimova, CoMo/SBA-15 catalysts prepared with EDTA and citric acid and their performance in hydrodesulfurization of dibenzothiophene, Appl. Catal. B: Environ. 147 (2014) 879-887.

[32] S. Eijsbouts, L. Van den Oetelaar, R. Van Puijenbroek, MoS_2 morphology and promoter segregation in commercial Type 2 Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 hydroprocessing catalysts, J. Catal. 229 (2005) 352-364.

[33] K. Xu, Y. Li, X. Xu, C. Zhou, Z. Liu, F. Yang, et al., Single-walled carbon nanotubes supported Ni-Y as catalyst for ultra-deep hydrodesulfurization of gasoline and diesel, Fuel 160 (2015) 291-296.

[34] F. Rashidi, T. Sasaki, A. M. Rashidi, A. Nemati Kharat, K. J. Jozani, Ultradeep hydrodesulfurization of diesel fuels using highly efficient nanoalumina-supported catalysts: Impact of support, phosphorus, and/or boron on the structure and catalytic activity, J. Catal. 299 (2013) 321-335.

[35] W. Zhou, Q. Zhang, Y. Zhou, Q. Wei, L. Du, S. Ding, et al., Effects of Ga- and P-modified USY-based NiMoS catalysts on ultra-deep hydrodesulfurization for FCC diesels, Catal. Today 305 (2018) 171-181.

[36] S. Shan, H. Liu, Y. Yue, G. Shi, X. Bao, Trimetallic WMoNi diesel ultra-deep hydrodesulfurization catalysts with enhanced synergism prepared from inorganic–organic hybrid nanocrystals, J. Catal. 344 (2016) 325-333.

[37] L. Peña, D. Valencia, T. Klimova, CoMo/SBA-15 catalysts prepared with EDTA and citric acid and their performance in hydrodesulfurization of dibenzothiophene, Appl. Catal. B: Environ. 147 (2014) 879-887.

[38] T. Kabe, W. H. Qian, S. Ogawa, A. Ishihara, Mechanism of Hydrodesulfurization of Dibenzothiophene on Co-Mo/Al_2O_3 and Co/Al_2O_3 Catalyst by the Use of Radioisotope 35S Tracer, J. Catal.143 (1993) 239-248.

Table Captions:

Table 1 Acidity for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Table 2 HRTEM statistic results of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Table 3 XPS results of sulfurized Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.

Table 4 Properties of testing feedstocks for HDS reaction.

Table 5 Comparison of HDS results for different catalysts.

Table 6 Comparing the catalytic activity of the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst and other reported catalysts.

Table 7 Reaction conditions and results in hydrotreating unit.

Table 1 Acidity for Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Catalysts	Total acidity (μmol/g)	Brönsted (μmol/g)	Lewis (μmol/g)	B/L ratio
Co-Mo-C/mesoporous γ-Al_2O_3	544	139	405	0.34
Co-Mo/mesoporous γ-Al_2O_3	487	44	443	0.10

Table 2 HRTEM statistic results of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Properties	Co-Mo/mesoporous γ-Al_2O_3	Co-Mo-C/mesoporous γ-Al_2O_3
Maximum slab length (nm)	17.3	11.1
Average slab length (nm)	9.5	4.8
Percentage of 1-2 layers	75.2	47.9
Percentage of 3-5 layers	20.1	49.7
Percentage of >5 layers	4.7	2.4

Table 3 XPS results of sulfurized Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.

Catalyst	Co-Mo/mesoporous γ-Al_2O_3	Co-Mo-C/mesoporous γ-Al_2O_3
$Mo^{4+}/(Mo^{4+}+Mo^{5+}+Mo^{6+})$ (%)	65.88	75.03
S/Mo	1.74	1.78
Mo $3d_{5/2}$ BE (eV)	228.8	228.5
Co $2p_{3/2}$ BE (eV)	780.1	778.4

Table 4 Properties of testing feedstocks for HDS reaction.

Feedstock	Diesel oil
Density at 20°C (g/cm^3)	0.8397
Distillation range (°C)	
IBP (10%)	151/189
30%/50%	242/286
70%/90%	312/352
95%/FBP	366/378
Sulfur content (μg·g^{-1})	9000
Nitrogen content (μg·g^{-1})	150
4,6-DMDBT content (μg·g^{-1})	192

Table 5 Comparison of HDS results for different catalysts.

Feedstock	Diesel oil			
Catalyst	Co-Mo-C/mesoporous γ-Al_2O_3		Co-Mo/mesoporous γ-Al_2O_3	
HDS conditions				
Average reaction temperature (^oC)	360	370	360	370
Hydrogen pressure (MPa)	6.0	6.0	6.0	6.0
Space velocity (h^{-1})	0.77	0.77	0.77	0.77
Hydrogen/oil ratio	400	400	400	400
Sulfur content ($\mu g \cdot g^{-1}$)	7.4	4.0	12.0	7.0
Nitrogen content ($\mu g \cdot g^{-1}$)	2.4	2.2	5.0	4.0
4,6-DMDBT content ($\mu g \cdot g^{-1}$)	4.2	2.5	8.2	4.6

Table 6 Comparing the catalytic activity of the Co-Mo-C/mesoporous γ-Al_2O_3 catalyst and other reported catalysts.

Catalysts	Sulfur Concentration (ppm)	Conversion (%)	Temperature(^oC)	Stability (h)	Reference
Co-Mo-C/mesoporous γ-Al_2O_3	9000	99.9	358	5000	This work
CoMoPB/nanoAl_2O_3	13500	99.9	350	-	[34]
PGaHUSY	2259	99.7	360	-	[38]
WMoNi-HHD	3904	99.5	360	500	[37]
WMoNi/Al_2O_3	-	96.0	360	-	[10]
CoMo/SBA-15	2160	77	3000	-	[36]
Co-Mo/Al_2O_3	4000	67	3000	-	[35]

Table 7 Reaction conditions and results in hydrotreating unit.

Catalyst	Co-Mo-C/mesoporous γ-Al_2O_3	
Diesel	Feedstock	Product
Density at 20^oC (g/m^3)	839.0	831.6
Distillation range (D86, ^oC)		
IBP/10%	158/191	175/198
30%/50%	233/275	232/274
70%/90	313/349	311/348
95%/FBP	363/367	362/365
Sulfur content ($\mu g \cdot g^{-1}$)	9000	7.8

Figure Captions:

Fig. 1 Schematic process flow diagram of 3000 kt/a industrial-scale diesel ultra-deep hydrodesulfurization.

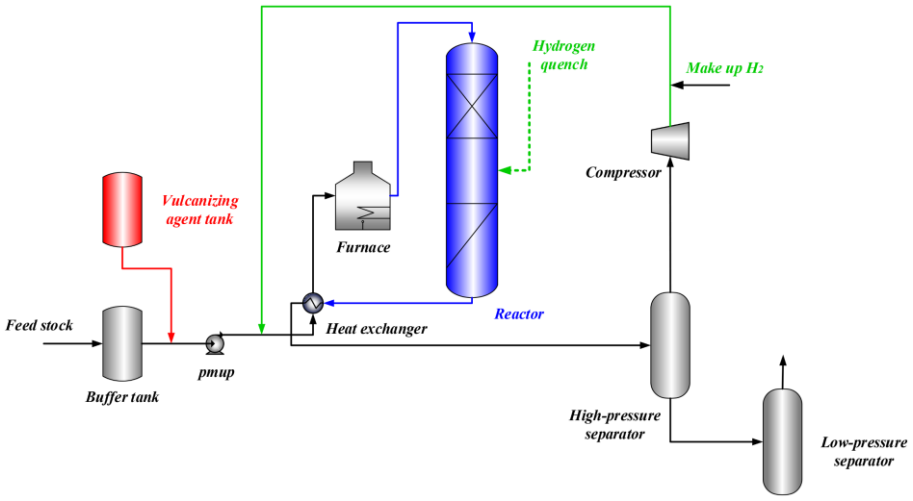
Fig. 2 XRD patterns (a) of mesoporous γ-Al_2O_3 support and N_2 physisorption (b) of catalysts.

Fig. 3 H_2-TPR spectra of Co-Mo/mesoporous γ-Al_2O_3 and Co-Mo-C/mesoporous γ-Al_2O_3 catalyst.

Fig. 4 Typical HRTEM of Co-Mo/mesoporous γ-Al_2O_3 (a) and Co-Mo-C/mesoporous γ-Al_2O_3 catalysts (b).

Fig. 5 Industrial-scale 3000 kt/a stability evaluation (a) in a hydrotreating plant (b).

Fig. 6 N_2 adsorption-desorption isotherms of fresh, deactivated and regenerated Co-Mo-C/mesoporous γ-Al_2O_3 catalysts.



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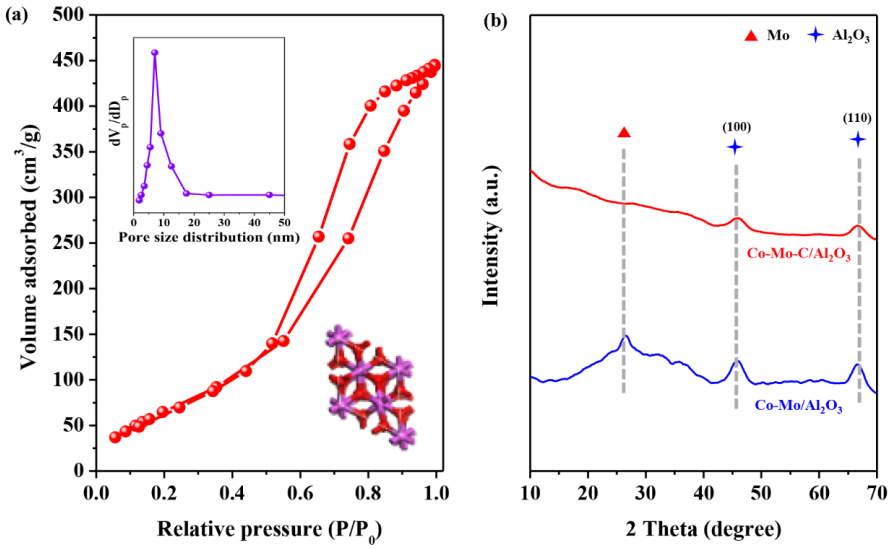

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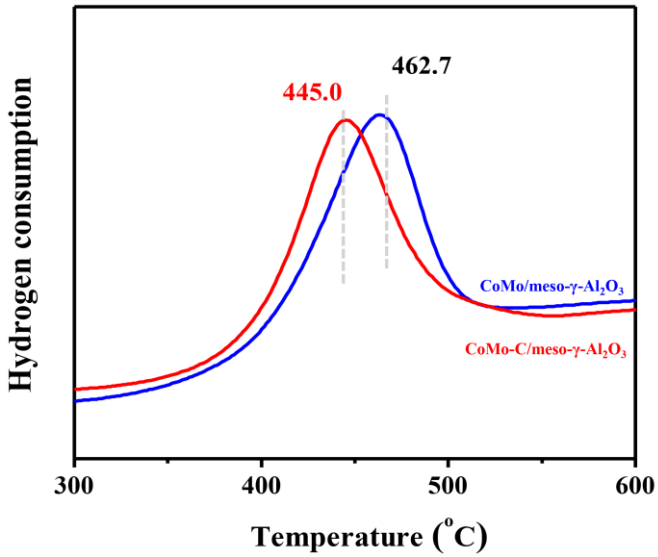

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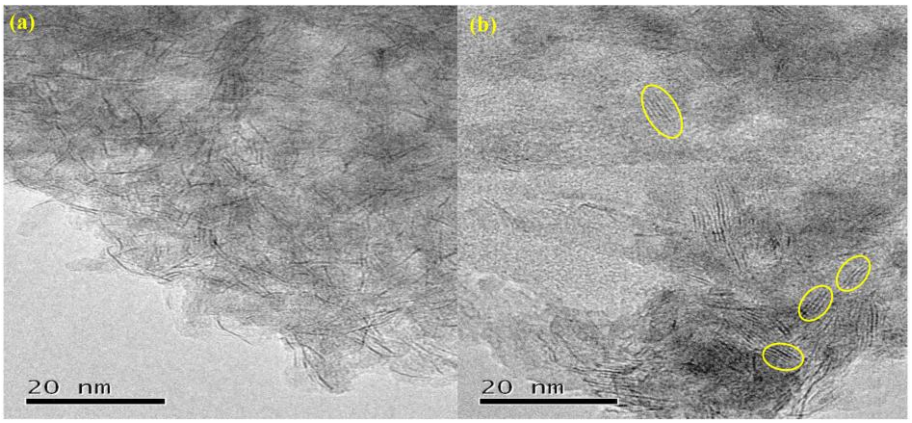

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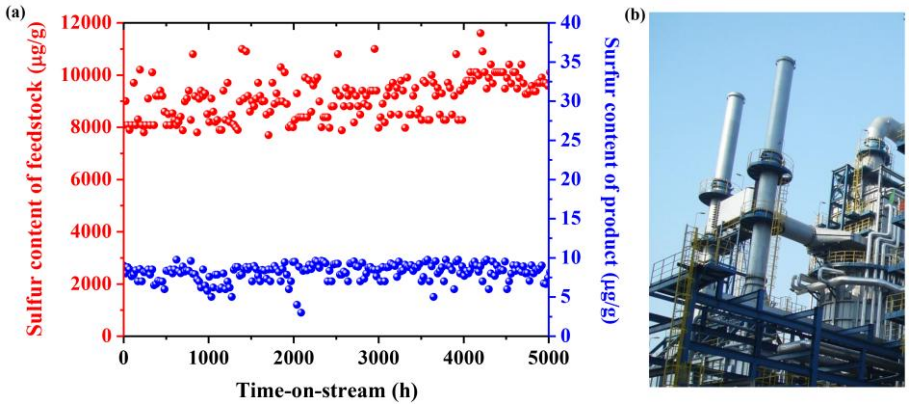

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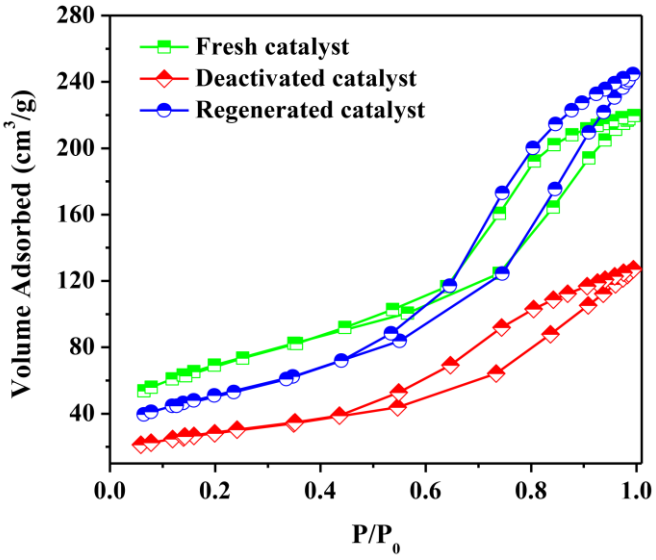

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