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A comparative study on the *ex situ* and *in situ* presulfurization of hydrotreating catalysts

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ABSTRACT

An improved *ex situ* presulfurization (EPRES) technique is developed for transforming metal oxides of hydrotreating catalyst to the corresponding metal oxy-sulfides/sulfides. The process involves preliminarily dispersing an organo-nitrogen substance onto the oxide catalyst, introducing elemental sulfur together with an organic solvent, and a subsequent multi-step heat treatment. The physicochemical properties of the obtained EPRES catalyst with respect to the *in situ* presulfurization (IPRES) counterpart are studied by X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), and high pressure differential thermal analysis (HPDTA). XRD analysis indicates that the organo-nitrogen substance facilitates metal oxy-sulfide to disperse uniformly on γ-Al_2O_3 and the resulting metal oxy-sulfide species turn to be rather structurally amorphous. XPS together with TEM investigations reveal that higher content of active surface NiMoS/MoS_2 species, less metallic Ni fraction, and uniformly dispersed surface S species are the features of EPRES catalyst, well correlated with its higher catalytic activity. HPDTA study indicates that the concentrative exothermic effect can be effectively minimized by adopting mixed sulfurizing agents and appropriate introducing manner. The degree of sulfurization can also be obviously enhanced by tuning thermo-treatment. The EPRES process can considerably shorten the start-up procedure in pilot plant test and a wide range of commercial practices, exhibiting its economical advantage and low environmental impact.

1. Introduction

For selective removal of sulfur and nitrogen compounds, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the two important reactions in hydrotreating of heavy oil feedstock containing high concentrations of sulfur and nitrogen compounds in refineries. The hydrotreating catalysts are commonly sulfided Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3. Promoters include B, P, Ti, Zr, K and rare earth oxides, which may be added to lower the acidity of the catalyst and/or improve Mo dispersion and sulfidability. Presulfurization is an essential process for activation of a hydrotreating catalyst in the oxidic form [1,2]. The conventional process, i.e., *in situ* presulfurization (IPRES), is used to sulfurize the pre-loaded catalyst in a reactor by introducing a sulfurizing agent. On the contrary, *ex situ* presulfurization (EPRES) is the process in which the catalyst is sulfurized or partially sulfurized before loading the catalyst into reactor. Compared with *in situ* sulfurization, *ex situ* presulfurization takes much shorter period of treating time, hence significantly increases production efficiency [3–5].

The impregnation method was mainly used for introducing sulfurizing agent, and different kinds of solvents are essential to dissolve the sulfurizing agents. Since 1980s' different *ex situ* presulfurization techniques have been accomplished. Typical examples are those developed by EURECAT (France) [6–11], CRITEIRON (U.S.A.) [12,13], AKZO (Netherlands) [14,15], and TRICAT (Germany) [16,17]. EURECAT first adopted organic polysulfide as sulfurizing agent to achieve presulfurization in two steps [3,6–8]. Later on EURECAT also used $(NH_4)_2S$ as sulfur-containing additives [9], and elemental S [10] or H_2S [11] as the sulfurizing agents. The impregnation method was mainly used for introducing sulfurizing agent, and different kinds of solvents are essential to dissolve the sulfurizing agents. CRITEIRON used elemental S as the sulfurizing agent and high boiling point oil or liquid hydrocarbon as the solvent [12,13]. In some cases, however, the temperature rise in presulfurization process was rather significant. AKZO developed the *ex situ* presulfurization process in moving-bed reactor using water solvable sulfur compounds in liquid phase [14] and impregnated sulfur-containing additives plus H_2S in gas phase [15]. TRICAT developed the *ex situ* presulfurization technique, called as XPRESS, in which H_2S served as the sulfurizing agent and the process was operated in a moving-

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bed reactor [16,17]. The best treating temperature was found to be 540 °C.

For the *ex situ* presulfurization catalyst, one major concern is how to effectively reduce the concentrative release of heat during its activation process [18], and furthermore, to improve the level of sulfur content of catalyst. In order to control the concentrative release of presulfurization heat effectively, it is very helpful to monitor the exothermic effect of *ex situ* presulfurization process accurately by suitable means. As a matter of fact, there is no commercially available apparatus which can be operated under the *ex situ* presulfurization condition to which high pressure and high concentration of corrosive H_2S are applied. We had systematically studied catalyst design, preparation, and evaluation of different hydrotreating catalysts with the aim of improving catalyst activity and stability in both laboratory scale and industry practice [19–21]. Special attention has been paid to the effect of *ex situ* presulfurization with respect to *in situ* presulfurization of oxidic catalyst precursor on catalyst property [20,21]. After the years of efforts, an improved EPRES process was successfully developed to fulfill the optimized sulfurization of oxide precursor. Moreover, the exothermic effect of *ex situ* presulfurization, determined by means of anti-corrosion high pressure differential thermal analysis (HPDTA) established in our laboratory, was found to be notably smaller than that of *in situ* sulfurization process.

Most published papers are mainly focused on the activity of various catalysts and the involved reaction mechanisms, with limited ones on detailed catalyst preparation, seldom on the comparison between the *in situ* and *ex situ* presulfurization techniques. In the present study, the investigation of X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), and high pressure differential thermal analysis (HPDTA) were conducted to characterize our EPRES catalyst with respect to the *in situ* presulfurization (IPRES) counterpart, to clarify the difference of their structures, the dispersion and the state of the active surface NiMoS/MoS_2 species, and then to correlate the physicochemical properties with their catalytic activities. Hopefully we can gain some new insights into the presulfurized catalysts and some hints for further enhancing the degree of sulfurization, and minimizing the concentrative exothermic effect with our developed *ex situ* sulfurization technique.

2. Experimental

2.1. Catalyst preparation and presulfurization

The EPRES catalyst was prepared by homogeneously dispersing sulfur-containing agents onto the commercial hydrotreating metal oxide catalyst FH-5A (developed by Fushun Research Institute of Petroleum and Petrochemicals, China) with catalyst formulation of Ni–Mo/Al_2O_3 (Ni/Mo ratio = 0.24). The detailed catalyst preparation involved the following three procedures [19]: (1) dipping the oxide catalyst precursor in a solution of an organo-nitrogen compound (such as hydrocarbyl amine and organic ammonium) in an amount of 2–10% by weight of catalyst; (2) loading sulfur by introducing elemental sulfur or organic sulfides together with hydrocarbon oil used separately or in combination with organic carboxylic substance. Preferably, they are mixed together since it is advantageous to solve the problem of concentrative exothermic phenomenon; (3) thermal treating at 110 °C for 7 h, then 160 °C for 4 h, and finally 200 °C for 4 h. Heat treatment can be carried out in an oxygen-containing atmosphere having an oxygen content of 0.17 vol.%. As illustrated in Fig. 1, the role of the introduced organo-nitrogen substance is to increase the diffusion of sulfur into catalyst pores and therefore achieve uniform sulfur dispersion. Moreover, the presence of organo-nitrogen substance can restrain the reaction of sulfur with hydrogen-containing compound (e.g., hydrocarbon) to form H_2S, not only increases the sulfur utilization efficiency but also reduces the environmental impact of H_2S product. The adopted multiple step heat treatment can optimize various state of the intermediate compound $MeO_{(x-y)}S_y$, leading to a reduction in the release of concentrated exothermic heat during start-up procedure [20].

The IPRES catalyst was prepared according to a conventional procedure. For comparison, exactly the same Ni–Mo/Al_2O_3 (Ni/Mo ratio: 0.24) as that EPRES catalyst was adopted. The *in situ* presulfurization was conducted using CS_2 as sulfurizing agent (2% concentration) mixed in the start-up oil feed.

2.2. Start-up procedures and catalyst evaluation

In laboratory study, the start-up procedure and catalyst evaluation was performed in a fixed bed stainless steel reactor, with a length of 1300 mm and inner diameter of 28 mm. The start-up procedure of the EPRES catalyst comprises the following steps: (1) purge the unit with nitrogen until the oxygen level is below 0.5 vol.%; (2) pressurize the unit with hydrogen to 2.0–6.0 MPa and have a pneumatic test; (3) raise the temperature from ambient at a rate of 10–25 °C/h and start dosing of liquid flow as the reactor temperature is beyond 110 °C; (4) continuously raise the temperature to 320 °C, and then maintain for at least 1 h; (5) switch to operating conditions, and then stop liquid recycle; (6) switch to the operating oil feed.

A typical start-up procedure of the IPRES catalyst involves the following steps: (1) purge the reaction system with nitrogen till the concentration of oxygen is less than 0.5 vol.% and then have a pneumatic test at 3.4 MPa; (2) perform catalyst drying with nitrogen at 200 °C for 4 h; (3) presulfurize through a wet-treatment of catalyst with a mixture of CS_2 and light diesel oil at 150 °C for 2 h; (4) gradually increase the temperature to 230 °C at a rate of 10–25 °C/h and maintain for 10 h; (5) further increase temperature to 320 °C at the same rate and maintain for another 10 h. Sulfurization is finished as the concentration of H_2S in recycle hydrogen reaches about 1.0 vol.%; (6) introduce the oil feed gradually and finish the start-up.

The activity of the EPRES catalyst as well as the counterpart IPRES catalyst was subsequently evaluated under the following

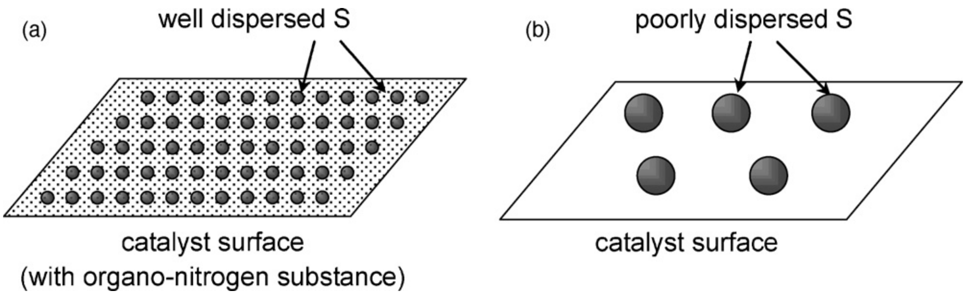

Fig. 1. The illustration of sulfur dispersion on the catalyst precursor (a) with and (b) without the organo-nitrogen substance.

conditions: liquid hourly space velocity (LHSV) = $2.5\,h^{-1}$; hydrogen partial pressure = 3.4 MPa; temperature = 350 °C, and volume ratio of hydrogen to oil feedstock = 350. The feedstock is Kuwait blended diesel with sulfur and nitrogen contents of 11,640 μg/g and 250.4 μg/g, respectively.

A scale-up study was performed in an adiabatic pilot plant with the capacity of 60 L. The height and diameter of the reactor is 2000 mm and 180 mm, respectively. The conditions adopted for start-up procedure and catalyst evaluation are the same as indicated above.

2.3. Catalyst characterization

The TEM images of the EPRES and IPRES samples were obtained using a FEI-Technai-20 transmission electron microscope. XRD analysis was performed on a Rigaku D/max 2500 X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 0.1541$ nm) which was operated at 40 kV and 80 mA. The measured 2θ range is 10–70°, with a scan speed of 8°/min. XPS measurement of EPRES and IPRES catalysts was performed on a VG Multilab 2000 spectrometer using Mg Kα radiation. The binding energies (BEs) were calibrated against the C 1s signal (284.6 eV) of contaminant carbon. The surface composition of elements was estimated on the basis of curve-fitting of spectra and having the corresponding peak areas normalized by using the XPS PEAK FIT software. The anti-corrosion HPDTA technique was applied for measuring the exothermic effect of EPRES catalyst in the lab scale unit during start-up procedure. The intensity of exothermic effect of catalyst is related to the amount of heat released during start-up, and the exothermic effect of the EPRES catalysts subject to treatments at various temperatures in the lab scale unit has been quantified by means of HPDTA. Note that under the HPDTA measuring conditions (RT-450 °C; heating rate: 10 °C/min; pressure: 3.5 MPa H_2) there was no loss of sulfur from the EPRES catalysts observed. For the 60-L pilot plant and commercial unit operations, temperature difference between the inlet and outlet of catalyst bed is employed to indicate the exothermic effect.

3. Results and discussion

3.1. Sulfur utilization ratio

The hydrotreating catalysts are commonly sulfided Co–Mo/Al_2O_3 or Ni–Mo/Al_2O_3. Promoters include B, P, Ti, Zr, K and rare earth oxides, which may be added to lower the acidity of the catalyst and/or improve Mo dispersion and sulfidability. Mo and Ni are regarded as the active species in hydrotreating catalysts [1]. The form of active metal species in the sulfurized catalysts is rather complicated, and the precise structure of the sulfided catalyst is still under debate. Nominally, MoS_2, Ni_3S_2, and mixed sulfides (Co–Mo–S, etc.) are some of examples. The key point with the EPRES process of hydrotreating catalysts is to take advantage of using combined sulfur-containing agents as the sulfur source and to reduce the loss of sulfur from the EPRES catalysts.

The loss of sulfur from the EPRES catalysts is closely related to the sulfur utilization ratio [21]. Activation of the EPRES catalyst is achieved in a hydrogen stream, and the sulfur specimen in the EPRES catalyst could be converted to other compounds in the following manners: (a) reacting with the metal components of catalyst; (b) reacting with hydrogen to generate hydrogen sulfide which can enter hydrogen stream and involve recycling; and (c) losing away from the system. The effective sulfur utilization ratio of an EPRES catalyst (*Cons*) can be defined as the following equation:

$$Cons = \frac{M_E}{M_S} \times 100\%$$

where M_S is the total amount of sulfur in sulfur-containing agents for EPRES and M_E is the amount of sulfur existing in EPRES catalyst.

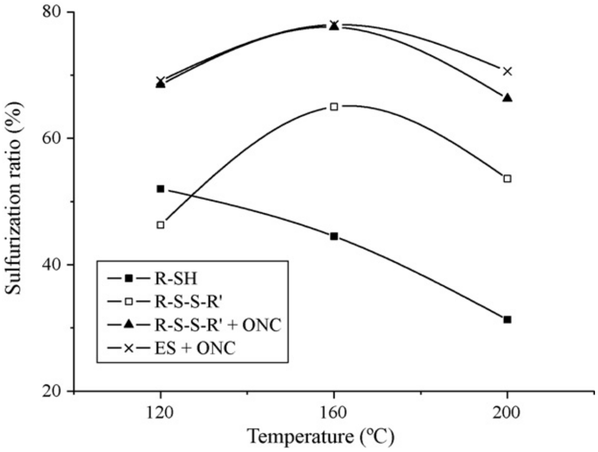

Fig. 2. Sulfur utilization ratios of the catalysts prepared using certain sulfur-containing agents with and without organo-nitrogen compound (ONC) at various treating temperatures.

The studies by Vanrysselberghe [1] and Berrebi et al. [6–8] revealed that the rate of catalyst sulfurization is dependent on the molecular form of the sulfurizing agent used and the rate of decomposition of such sulfurizing compound. According to the definition of effective sulfur utilization ratio, a higher ratio signifies a higher proportion of sulfur in sulfurizing agent reacts with the oxide precursor. In order to enhance the degree of the desired reaction and to achieve the highest effective sulfur utilization ratio, the following countermeasures have been taken into consideration: (1) the use of different sulfur-containing agents with or without organo-nitrogen compound has been explored; (2) an organo-nitrogen compound has been specially applied in the present study to enhance the dispersion of sulfurizing agent of elemental S over the surface of oxide precursor, as schemed in Fig. 1, as a consequence, the well dispersed sulfurizing agent (elemental S) can more easily react with the oxide precursor; (3) sulfurizing temperature is another critical factor to determine the sulfur utilization ratio. Heat treatment at different temperature can bring about certain degree of interaction between sulfurizing agent and oxide precursor, resulting in different sulfur utilization ratio. If a multi-heat treatment is adopted, the sulfurizing agent could be preserved to highest level over surfaces and react with oxide species more efficiently. During activation of the EPRES catalyst, some sulfur specimen in the EPRES catalyst could react with hydrogen to generate hydrogen sulfide. However, the EPRES process makes the precursor of transition metal oxides converted into oxy-sulfide ($MeO_{(x-y)}S_y$). Therefore, it prevents severe sulfurization as occurs in the IPRES process, and thus can efficiently reduce concentrative release of reaction heat during the start-up procedure. As a result, the undesired reaction (S species + $H_2 \rightarrow H_2S$) can also be significantly suppressed. Fig. 2 clearly indicated that the adoption of organo-nitrogen compound and appropriate heat treatment can notably increase the effective sulfur utilization ratio of EPRES catalyst.

3.2. Morphological and structural analysis

The TEM images of the EPRES and IPRES catalysts shown in Fig. 3 provide the morphological information with the two catalyst samples. One can observe that in the latter catalyst there is partial sulfide conglomeration while in the former sample there is no such phenomenon. The consequence results from different dispersion of sulfur species of sulfurizing agent on precursor surface and different degree of sulfurization of oxide precursor during *ex situ* or *in situ*

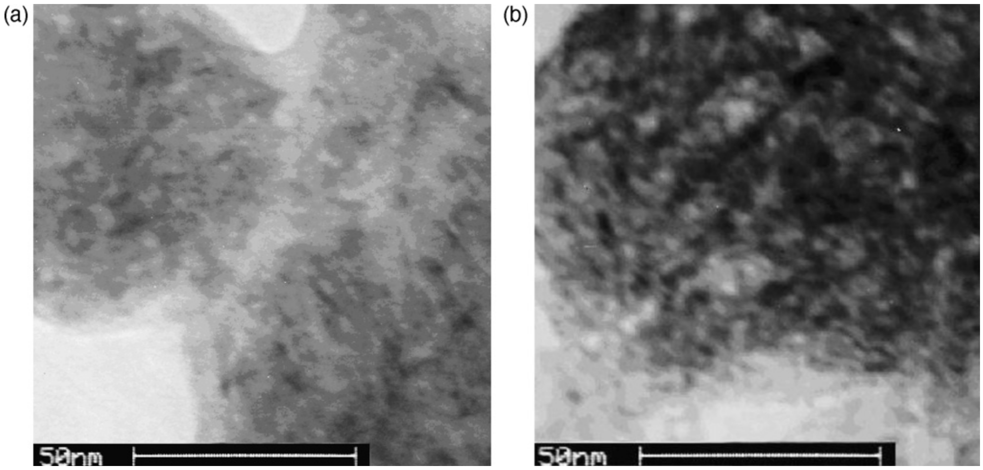

Fig. 3. TEM images of (a) the present EPRES catalyst and (b) the reference IPRES counterpart.

presulfurization procedure. Even in *ex situ* presulfurization, one can clearly see that different sulfurizing agents show considerable variation in sulfur utilization ratio as shown in Fig. 2, which suggests that, the dispersion and interaction of sulfur species in sulfurizing agents with oxide precursor can change significantly during the *ex situ* presulfurization procedure. The dispersion of sulfur species of R–SH could be comparably lower than that of RSSR', results in a lower degree of sulfurization reaction. In the case of introducing organo-nitrogen compound, the dispersion of sulfur could also be different upon the nature of sulfurizing agent. With the help of organo-nitrogen compound, the dispersion of elemental S can be significantly enhanced, which, in turn, results in uniform distribution of active sulfide component throughout the catalyst (Fig. 3) and higher effective sulfur utilization ratio (Fig. 2). Note that in the EPRES catalyst, sulfurizing agent(s) have already reacted with the oxide precursor to form oxy-sulfide ($MeO_{(x-y)}S_y$) (before start-up procedure) or sulfide (after start-up procedure) species, it is difficult to distinguish the dispersion state of un-reacted sulfurizing agent(s) in the TEM image.

The XRD results of the typical oxide precursor and the corresponding EPRES catalyst (Ni–Mo) are shown in Fig. 4. In the range of $2\theta = 35–70^\circ$, the peaks are ascribed to γ-Al_2O_3 support; while in the range of $2\theta = 10–35^\circ$, the broad peaks are attributed to the metal oxide precursor and the oxy-sulfuide. Note that the diffraction pattern ($2\theta = 10–35^\circ$) of the EPRES catalyst changes notably as compared with that of the oxide precursor; in addition, there is no pure Ni or Mo sulfide generated. The observations suggest that there are oxy-sulfide ($MeO_{(x-y)}S_y$) species formed in the EPRES catalyst before start-up procedure. With the replacement of oxygen atoms by sulfur ones in the oxide precursor during the *ex situ* presulfurization process, the local structural arrangement of the resulting oxy-sulfide species changes accordingly. From the XRD results one can infer that both supported oxide and oxy-sulfide specimen are highly dispersed on γ-Al_2O_3 and also rather structurally amorphous.

3.3. Surface elemental composition

The surface properties of the EPRES and IPRES catalysts are investigated by means of XPS. The XPS spectra of Ni component are shown in Fig. 5. There are two main peaks at ca. 855.4 eV observed on the EPRES and IPRES catalyst. In addition, two shoulders at around 852.2 eV are also observed. The main peaks can be ascribed to the NiMoS species while the shoulders to the metallic Ni. The shoulder of EPRES catalyst is much weaker than that of IPRES one, suggesting that there is much less metallic Ni species in the former catalyst. In other words, there is a higher proportion of active surface NiMoS species in the EPRES catalyst.

Fig. 6 illustrates the raw and curve-fitting XPS spectra of Mo^{4+} and Mo^{6+} species on the EPRES and IPRES catalysts. The surface elemental composition is estimated on the basis of spectral curve-fitting results and the normalized corresponding peak areas with the XPS PEAK FIT software. The following parameters are taken into consideration for spectral curve-fitting: (1) the

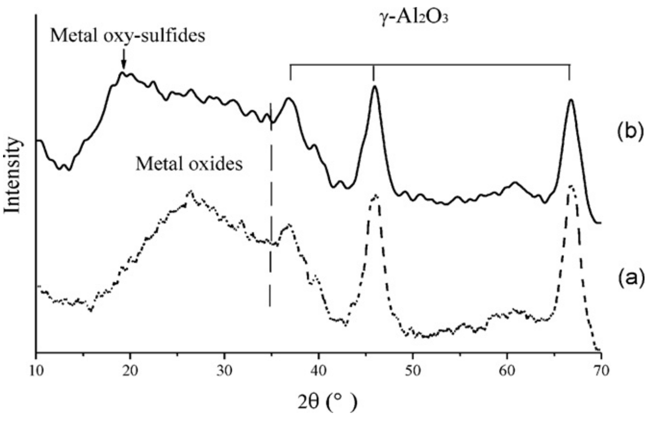

Fig. 4. XRD patterns of (a) the oxide precursor and (b) its corresponding EPRES catalyst (Ni–Mo).

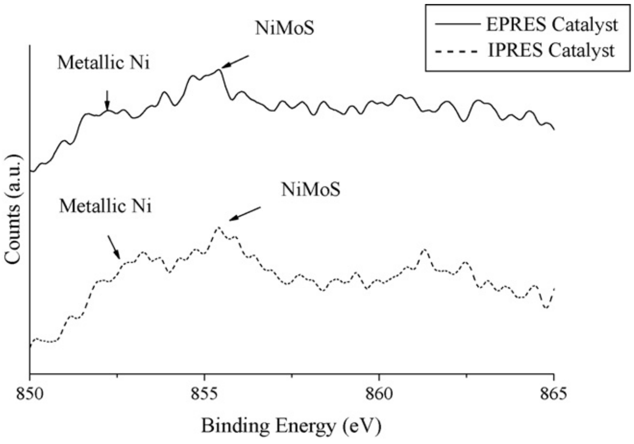

Fig. 5. XPS spectra of surface Ni species on the EPRES and IPRES catalysts.

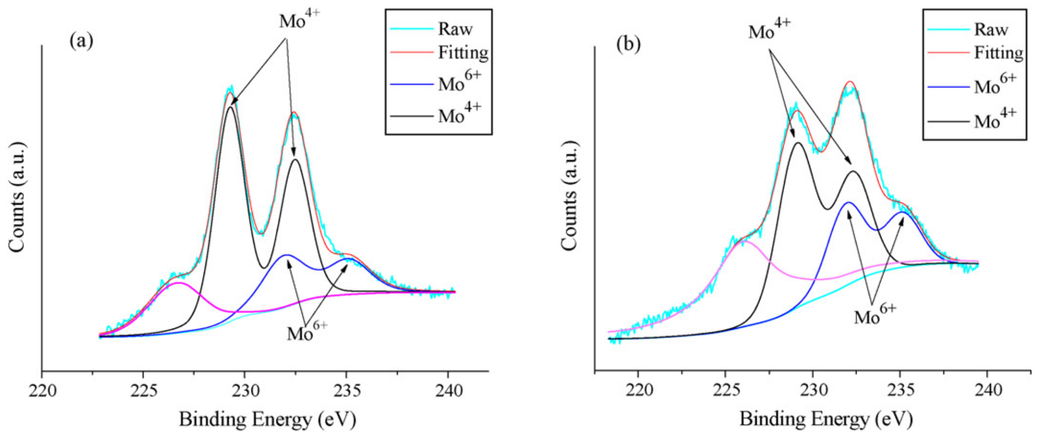

Fig. 6. The raw and curve-fitting XPS spectra of Mo^{4+} and Mo^{6+} species on (a) the EPRES and (b) IPRES catalysts.

binding energy of $Mo3d_{5/2}$ for Mo^{6+} and Mo^{4+} species is in the range of 232.0–232.4 eV and 228.7–229.2 eV, respectively [22]; (2) $\Delta E_b = E_b(Mo3d_{3/2}) - E_b(Mo3d_{5/2}) = 3.2$ eV; and (3) the FWHM ratio of two peaks for Mo^{6+} and Mo^{4+} species is 1:1. The Mo^{4+} content is determined according to the formula: $X\,(Mo^{4+})\,(\%) = [\text{Area}\,(Mo^{4+})/\text{Area}\,(Mo^{4+}) + \text{Area}\,(Mo^{6+})] \times 100\%$. The resulting Mo^{4+} content can also reflect sulfurization degree or level of different catalysts. It is observed that the present EPRES sample shows notably higher Mo^{4+} content (74%) than the IPRES counterpart (66%), indicating a higher degree of sulfurization achieved in the former catalyst. The XPS spectra of surface S species for the EPRES and IPRES catalysts are shown in Fig. 7. The S^{2-} species is dominated in both catalysts. Note that, however, the surface atomic ratio of sulfur to aluminium (S/Al) of the EPRES catalyst is found to be 0.27 while that of IPRES catalyst only 0.16, implying highly uniform dispersion of surface sulfur species in the EPRES sample. Higher degree of sulfurization results in higher content of active surface $NiMoS/MoS_2$ species and less fraction of metallic Ni, together with highly uniform dispersion of surface S species which are all favorable features for better catalyst activity.

Shown in Fig. 8 are the raw and curve-fitting XPS spectra of Mo^{4+} and Mo^{6+} species on the EPRES samples subject to different thermo-treatments (before start-up procedure). One can see that: (i) without a start-up procedure, only oxy-sulfuide ($MeO_{(x-y)}S_y$) is formed in the EPRES sample, and the degree of sulfurization is relatively low; (ii) thermo-treatment has a significant impact on the sulfurization of oxide precursor: only 20 °C – increase in temperature can notably enhance the Mo^{4+} content – an indicative of enhanced sulfurization level.

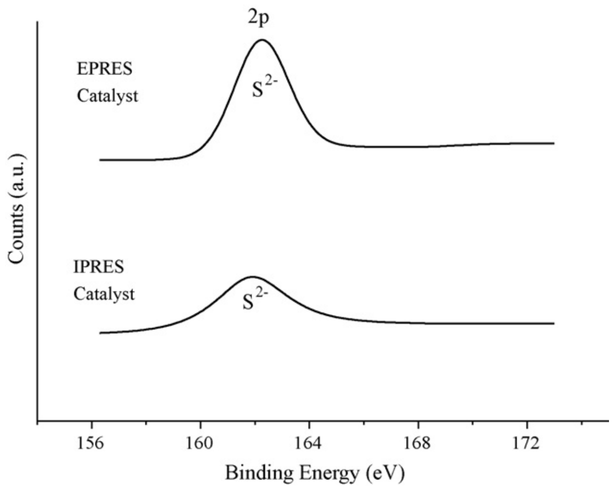

Fig. 7. XPS spectra of surface S species on the EPRES and IPRES catalysts.

3.4. Sulfur-retaining ratio and other physical characteristics

The sulfur-retaining ratio, defined as the ratio of the sulfur combining with EPRES catalyst to the total sulfur in feed and hydrogen passing through the catalyst bed, is the parameter determining the sulfurizing efficiency of catalyst. Some of sulfur specimen are decomposed and may be further converted into other compounds during the start-up procedure, which in turn has an impact on the characteristics of catalyst such as pore volume and specific surface area. The pore volume recovery ratio of the EPRES catalysts is defined as a relation of the recovered pore volume to the initial catalyst pore volume. The specific surface area recovery ratio and the average pore diameter recovery ratio are defined in the similar way. Fig. 9 shows the sulfur-retaining ratio and the pore volume (or specific surface area) recovery ratios of the EPRES catalyst and reference catalyst (a previous generation EPRES-type catalyst) under the same conditions. It is observed that the recovery ratio of pore volume (or specific surface area) of the present EPRES catalyst is comparable to those of the reference catalyst, while the sulfur-retaining ratio of the former is much higher than the later.

The extent of replacing oxygen atoms with sulfur ones can be referred to the degree of sulfurization:

$$a = \frac{W_E}{W_S} \times 100\%$$

where W_E is the actual amount of sulfur deposited, and W_S is the theoretical weight of sulfur replaced. The degree of catalyst sulfurization is closely related to the metal content in a catalyst. For the Ni–Mo bi-metal components of a catalyst, $W_S = W_S{}^{(Ni)} + W_S{}^{(Mo)}$. It is generally accepted that a rise in the degree of catalyst sulfurization can enhance the hydrotreating activity.

The EPRES catalyst can release hydrogen sulfide during its activation to achieve uniform sulfurization. Besides, activation can be carried out directly with the catalyst particle to ensure a sufficient catalyst sulfurization. The EPRES catalyst can be activated directly during start-up, and no subsequent drying process is needed. This leads to a shortened start-up period—a distinguished economic feature of the present EPRES catalyst.

A comparison for the characteristics of a typical EPRES catalyst and an IPRES one is summarized in Fig. 10. One can see that the utilization ratio of metal component of the EPRES catalyst was apparently higher than that of the IPRES one.

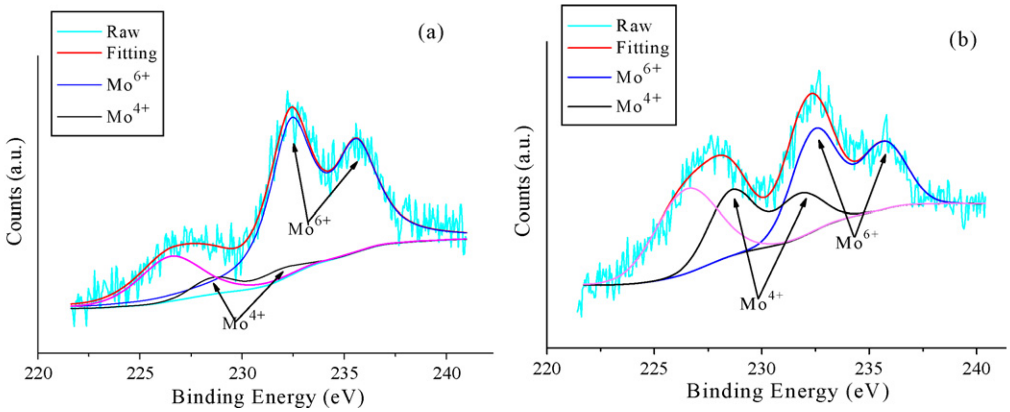

Fig. 8. The raw and curve-fitting XPS spectra of Mo^{4+} and Mo^{6+} species on the EPRES samples treated at (a) a specific temperature and (b) a temperature of 20 °C higher.

3.5. Exothermic effect

The sulfurization of oxide precursor is an exothermic reaction; therefore, the reaction must be painstakingly controlled to reduce concentrative heat release which may cause uncontrollable temperature rise in refinery and catalyst sintering. It is known that the exothermic effect of IPRES catalyst is significant, and such an issue could be resolved when an EPRES process is applied, especially in commercial application. The investigation on the exothermic effect of the EPRES catalysts subject to different treatments has been conducted and the results are illustrated in Fig. 11. In order to minimize the release of reaction heat, the sulfurization process can be operated in multi-steps, namely, consecutive treatments at different temperatures (from 110 °C to 160 °C and finally to 200 °C). From Fig. 11, one can clearly see that the strategy of such a multi-heat treatment is valid to achieve smaller exothermic effect. Thus the exothermic effect of an EPRES catalyst can be effectively minimized by tuning the presulfurizing treatment.

On the other hand, in case mixed sulfurizing agents were used for the reaction, one can also find that the way of introducing the sulfurizing agent(s) is critical for controlling the release of presulfurization heat. For instance, if two kinds of sulfurizing agents (RSSR' and elemental S with the weight percentage of 5.9% and 6.4%, respectively) were used at a time for presulfurization, the HPDTA results revealed that by changing the way of introducing RSSR' with respect to elemental S, the exothermic zone would be shifted toward lower temperature end by 5–10 °C, and the maximum temperature difference reduced from 12 °C to <7.8 °C. In the case of changing the way of introducing elemental S with respect to RSSR', an additional exothermic zone appeared at 200–230 °C, which averaged the release of sulfurization heat caused by RSSR' as well as elemental S, resulting in smaller temperature variation of <6.5 °C. Although the HPDTA measurements clearly demonstrate the exothermic effect of sulfurization can be effectively modified by applying the mixed sulfurizing agents and changing the manner of introduction, the details of thermo-chemical reactions are still unclear yet, and further investigation is valuable on this aspect.

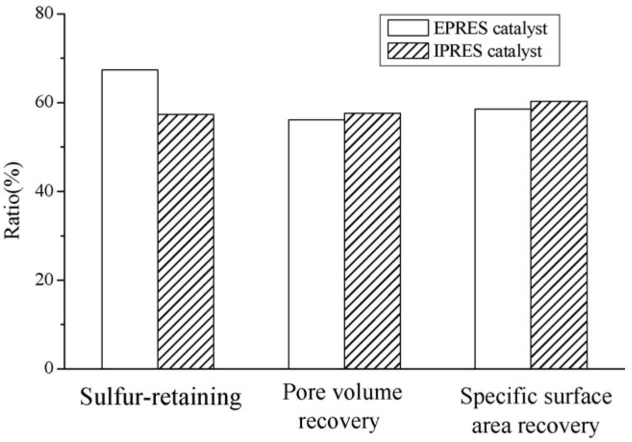

Fig. 9. Sulfur-retaining ratio and physical characteristics of the EPRES and IPRES catalysts.

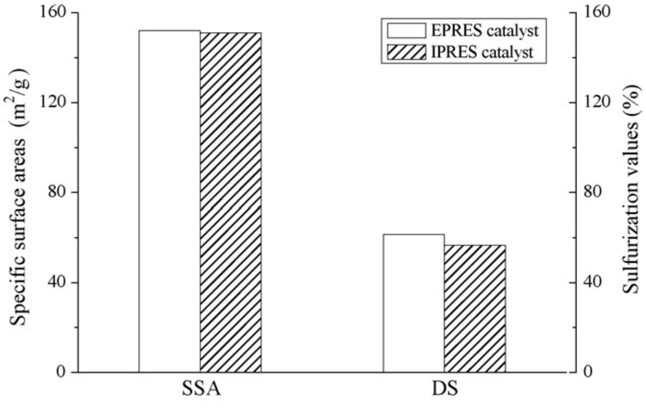

Fig. 10. Specific surface areas (m^2/g) and sulfurization values (a, %) of the EPRES and IPRES catalysts.

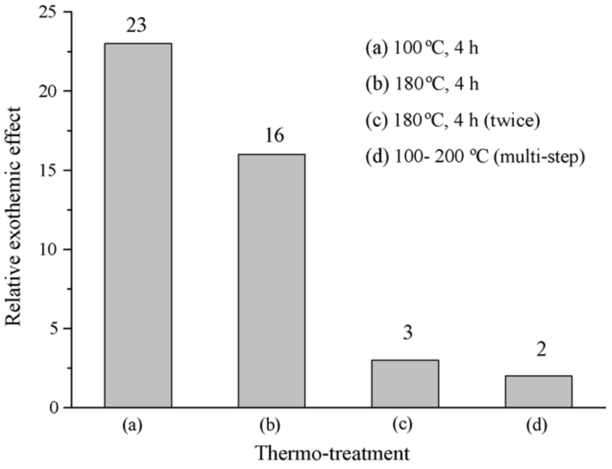

Fig. 11. HPDTA analysis of the EPRES catalysts subject to different heat treatments. Measuring conditions: temperature range, RT-450 °C; heating rate, 10 °C/min; pressure, 3.5 MPa H_2. (a) Heat treatment at 100 °C for 4 h; (b) heat treatment at 180 °C for 4 h; (c) heat treatment twice at 180 °C for 4 h; (d) multi-step thermo-treatment at 110 °C for 7 h, then 160 °C for 4 h, and 200 °C for 4 h.

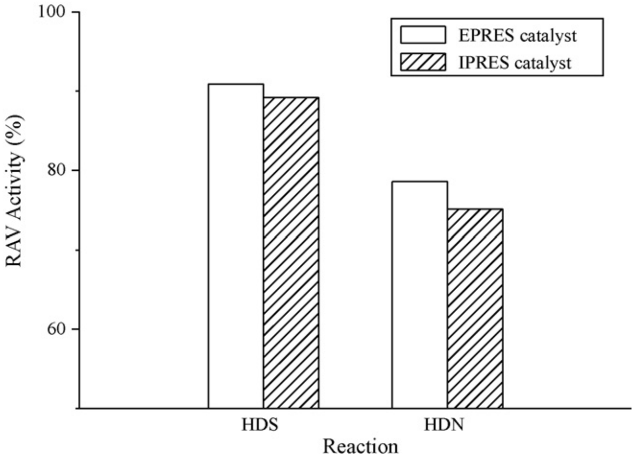

Fig. 12. Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities of the EPRES and IPRES catalysts. The feedstock of blended diesel: density = 0.85 g/cm^3, distillation range = 184–353 °C, sulfur content = 11640 μg/g, nitrogen content = 250.4 μg/g.

The two sulfurizing agents have different reactivity, and depending on the way of introduction (introduced at different sequence or simultaneously), the degree of sulfurization is different; as a result, the exothermic effect can be changed accordingly. By tuning the ratio of two sulfurizing agents and the way of introduction, sufficiently high degree of sulfurization with smaller exothermic effect could also be achieved.

3.6. Catalyst performance evaluation, pilot plants and commercial use

Higher degree of sulfurization leads to higher utilization ratio of metal component, and consequently, the higher activity of the catalyst. This is confirmed by the catalytic activities derived from the EPRES and the corresponding IPRES catalysts (Fig. 12).

The performance evaluation results in Fig. 12 indicate that the hydrodesulfurization and hydrodenitrogenation activities of the present EPRES catalyst are 90.8% and 78.6%, respectively, while that of the IPRES catalyst are 89.2% and 75.1%, respectively, under the same operating conditions (2.5 h^{-1} of LHSV, a hydrogen to oil volume ratio of 350, a reaction pressure of 3.4 MPa, and a reaction temperature of 350 °C). Based on performance evaluation and XPS measurement of the corresponding catalysts, one can infer that the higher-containing surface MoS_2 (76%) together with NiMoS species in the EPRES catalyst, vs. lower content surface MoS_2 (65%) plus NiMoS in the IPRES catalyst, may account for enhanced the HDS and HDN activity. The stability of EPRES as well as IPRES catalyst is investigated with a long period operation. The EPRES catalyst can be stabilized after at least 2000 h running, the same as the IPRES catalyst.

A scale-up study was performed in a 60-L pilot plant. The maximum temperature rise at the outlet with respect to that at the inlet of the catalyst bed during activation of the EPRES catalyst has proved to be a good measurement of the exothermic effect [23]. The temperature difference between the inlet and outlet of the catalyst bed during activation of the EPRES catalyst is illustrated in Fig. 13, which indicates that there is a steady rise in temperature of catalyst bed during start-up procedure of EPRES catalyst. It has been found that a shorter start-up period (40 h shorter) together with a steady and low temperature rise (14 °C in maximum) can be achieved in the start-up process of the present EPRES catalyst, which meets the requirements of commercial application.

After the issues of manufacture, storage and transportation for the EPRES catalyst have been addressed in the same way as for the conventional oxide catalyst (no need of N_2 protection), the EPRES catalyst was successfully operated for the first time in the hydrotreating unit of a commercial refinery. The present EPRES catalyst can be simply loaded into the reactor likewise the conventional oxide catalyst. Moreover, there is small temperature gradient between the inlet and outlet of catalyst bed.

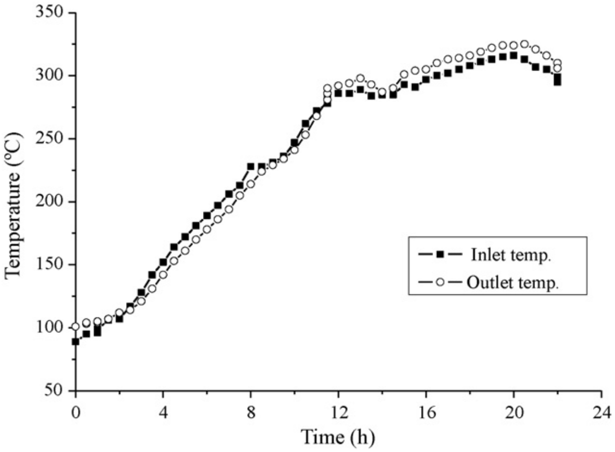

Fig. 13. Temperature profiles at the inlet and outlet of the catalyst bed in 60-L pilot plant during activation.

Unlike conventional catalysts, the use of the EPRES catalysts will cause much less environmental impact and exothermic effect during start-up procedure. Furthermore, it shortens the start-up period by 48 h. Thus, the application of the EPRES catalyst is not only environmentally friendly but also more economical for the refinery. Since year 2006 our developed EPRES catalyst has been applied in 20 commercial hydrotreating units of different types in China, with the treating capacity ranging from 15 × 10^4 t/a to 330 × 10^4 t/a.

4. Conclusions

In this research, the conventional EPRES technique is improved by introducing an organo-nitrogen substance together with elemental sulfur agent and a multi-step heat treatment. The presulfurized EPRES catalysts and the IPRES counterpart are systematically characterized by TEM, XRD and XPS, and correlated with their catalytic activities. The exothermic effect of the EPRES process is verified by HPDTA study. Remarkable features of the present EPRES catalyst are recognized: higher content of active surface NiMoS/MoS_2 species, less fraction of metallic Ni, and more uniform dispersion of surface sulfide species, which are the key factors accounting for the observed better HDS and HDN activities. The insights into the catalysts' surface and structure property provided the hints for further improving the current EPRES catalyst; namely, controlling the degree of sulfurization with appropriate thermo-treatment, and eliminating the concentrative exothermic effect with optimized sulfurizing agent(s) and better introducing manner. The EPRES process is proved to shorten the start-up procedure efficiently in pilot plant and commercial application, being more economical and environmentally friendly.

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