Effects of lanthanum and ethylenediamine tetraacetic acid on structure and hydrodesulfurization performance of Ni-W/TiO_2-Al_2O_3 catalyst

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Abstract: Using nickel-tungsten as active metals and TiO_2-Al_2O_3 as the support, Ni-W/TiO_2-Al_2O_3 catalysts for the hydrodesulfurization of heavy oil were prepared by wetness impregnation. The effects of the modification of lanthanum, ethylenediamine tetraacetic acid (EDTA)and La in cooperation with EDTA on the structure and hydrodesulfurization performance of the catalysts were investigated. The catalysts were characterized by XRD, BET, H_2-TPR and SEM. The results indicated that La and EDTA could weaken the interaction between support and active component, facilitate the reduction of active component, and benefit the formation of Ni-W-S phase. Addition of La or EDTA could increase the surface area and suppress the agglomeration of active metals on surface, forming smaller and highly dispersed active phase particles. The La, EDTA and combined La and EDTA modified catalysts possessed higher HDS activity than Ni-W sample, Ni-W-La-E catalyst had the highest HDS activity, and its thiophene conversion reached 99.7%.

Keywords: catalytic chemistry, hydrodesulfurization, lanthanum. ethylenediamine tetraaceticacid,

1. Introduction

With the intensification of the trend of crude oil, the proportion of high sulfur components in crude oil in the petrochemical industry is increasing. In order to protect the environment, countries around the world are constantly raising the standard of sulfur content in fuel oil. In 2017, the national V vehicle gasoline standard required sulfur content less than $10\mu g \cdot g^{-1}$, while some developed countries had more stringent requirements, using ultra-low sulfur fuel with sulfur content less than $5\mu g \cdot g^{-1}$.At present, hydrodesulfurization technology is mainly used at home and abroad to improve the sulfur content of oil products, but there is still a big gap between domestic hydrodesulfurization technology compared with foreign developed countries [1,2]. Therefore, it is urgent to develop a new type of high efficiency and high activity refined hydrodesulfurization catalyst.

Hydrodesulfurization catalysts with VIB, group metals (Mo and W) and group V metals (Ni and Co) as the active catalyst components and γ-Al_2O_3 as the carrier have been widely studied in the fields of petrochemical industry and coal chemical industry. Studies found that $TIiO_2$-Al_2O_3 as a new composite carrier, can promote the reduction of active metal oxide on the surface of the carrier, significantly improve the catalytic performance, is a kind of ideal composite carrier[3], among them, with NiW for active metal catalyst has the advantages of high hydrogenation activity and long service life, is a commonly used hydrodesulfurization catalytic system [4].Generally, the highly dispersed NiO and WO_3 species are mainly present on the NiW/TIO_2-Al_2O_3 catalyst carrier. In the sulfated NiW/TiO_2-Al_2O_3, the layered stacked WS_2 phase wafer are highly dispersed on the carrier surface; the auxiliary Ni atoms are dispersed at the coordination unsaturated position of the WS_2wafer, form the highly active Ni-W-S

Mixed-phase [5]. It is found that [6,7], rare earth elements added to the catalyst with its good reactivity, shows broad development prospects in the catalytic field with excellent physical and chemical performance. Among them, the introduction of rare earth element La can improve the high temperature stability and sintering resistance of γ-Al_2O_3, reduce the carbon accumulation on the surface of the catalyst, and improve the interaction force between the metal and the carrier [8], thus contributing to the formation

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of the highly active phase of the metal. The addition of chelating agent to the catalyst can improve the sulfation temperature and dispersion of the active components through the chelation with the active metal, which plays an important role in improving the catalytic performance of the catalyst [9].

The hydrodesulfurization catalyst with TIO_2-Al_2O_3 and Ni and W as active metal components, studied the modification of rare earth metal lanthanum (La), ethylenediaminetetraacetic acid (EDTA) and the modification of La-EDTA combination on the catalyst structure and hydrodesulfurization performance, and through X-ray diffraction, N $_2$adsorption-desorption, H_2-Program warming reduction and scanning electron microscopy characterized the catalysts.

2. As shown in the experimental section

2.1. Catalyst preparation

The TiO_2-Al_2O_3 composite vector was prepared by the sol–gel method. Add appropriate amount of nitric acid to 500 ML of deionized water; 20g of thin powder in clean beaker, add the above dilute nitric acid solution, stirring for 2h, and slowly add TiO_2 powder during sol, control pH=8, then standing, filtration, drying, roasting, forming, then TiO_2-Al_2O_3 composite carrier.

The catalyst was prepared by equal volume impregnation. (1) Weigh a certain amount of nickel nitrate and ammonium metasungstate in a beaker, dissolve a certain amount of EDTA in a certain amount of ammonia water, completely mix it and pour into the above beaker until it is completely dissolved. After set for 12h at room temperature, 100℃ was dried for 12h, 550℃ roasting for 5h, Made the EDTA modified catalyst, Note it to Ni-W-E; (2) Impregnated with Ni and Won the surface of the alumina carrier, Drying, roasting, Reimpregnated with a certain amount of lanthanum nitrate solution, And repeat the above drying, roasting procedure, To obtain the La modified catalyst, As Ni-W-La; (3) The alumina carrier is first soaked with EDTA, Ni, W, Drying, roasting, Impregnated with the La solution, Drying, roasting, To obtain the catalyst for the combined modification of LA and EDTA, Recoroted as Ni-W-La-E; (4)

Unmodified catalyst is denoted as Ni-W. Specifically, WO $_3$load mass fraction is 24%, NiO load mass fraction is 4%, La load mass fraction is 5%, and the quantity ratio of EDTA to Ni material is 1.5:1.

2.2. Catalyst characterization

The crystal phase structure was determined by TF-5500, CuKa, Ni filter, working voltage 50 kV, working current 100 mA, angular positioning rate 1500°·min~^{1}, step length 0.02, 20=10°~90°, and the measurement accuracy was 0.0002°.

The specific surface area and pore diameter of the carrier were distributed on the specific surface of 3H-2000PS2 type and aperture analyzer of Beide Instrument Technology (Beijing) Co., LTD. After the samples were evacuated at 671K for 2h, nitrogen adsorption test was conducted at liquid nitrogen temperature. The specific surface area was calculated by BET method and the pore diameter by BJH method.

H_2-TPR analysis was performed using Chembet, Cona Instruments, USA Pulsar TPR / TPD, TPR for the reduction performance of the catalyst.

Sample size and morphology were performed by Flex SEM, scanning electron microscope with operating voltage of 8 kV, the highest imaging resolution of 1μm and magnification of 5000~20000 times.

2.3. Catalyst activity evaluation

The catalyst was pre-sulfide with carbon disulfide/cyclohexanide solution (volume ratio 3:100) as a sulfide agent with a sulfide time of 4h and a sulfide temperature of 320℃. The hydrodesulfurization activity evaluation was conducted on a continuous fixed bed high-pressure microreactor with the model oil (sulfur content of thiophene and n-octane: 500mg·L^{-1}) as raw material, the reaction temperature was 300℃ and the reaction pressure was 3 MPa.

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3. Results and discussion

3.1. XRD

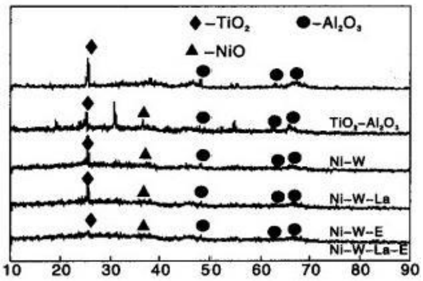

Figure 1. The XRD diagram of the TiO_2-Al_2O_3composite carrier and the different catalysts.

Figure 1 shows that the diffraction peaks of the four catalysts dipping the active fraction at 26.3°, 48.0°, 61.0°and 66.8°are consistent with the main diffraction peak of the TiO_2-Al_2O_3 composite carrier. With the incorporation of La, the peak intensity of Ni-W-La catalyst decreased at 26.3°and the half-peak width became larger, indicating that the rare earth metal La favors the reduction of crystallinity on the carrier surface. [10], probably because the metal La and part of TiO_2 bond to form Ti-O-La[11] during the drying and roasting of the sample. In addition, no obvious characteristic peak of La_2O_3 appeared in the Ni-W-E catalyst, indicating that the oxide of La was relatively evenly dispersed on the surface of the catalyst [12,13]. The NiO crystal phase diffraction peak of different intensity appeared from 37.2 °to 37.4°, among which, the unmodified Ni-W catalyst NiO was the strongest and relatively sharp.

After that, the NiO characteristic diffraction peak intensity of each catalyst decreased to different degrees, and the diffraction peak intensity of Ni-W-La and Ni-W-E catalyst was not much different, while that of Ni-W-La-E catalyst basically disappeared. This suggests the introduction of La or EDTA alone, as well as simultaneously

The introduction of La and EDTA both promoted the dispersion of NiO on the carrier surface and favored the formation of more active centers.

3.2. H_2-TPR

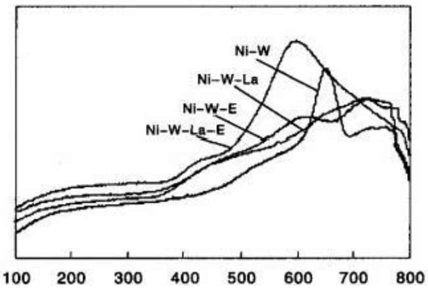

Figure 2 The H_2-TPR profiles of the different catalysts.

As can be seen from Figure 2, compared with Ni-W catalyst, Ni-W-La, NiO low temperature reduction peak of the catalyst to low temperature, and the low temperature reduction peak area increases, shows that the addition of rare earth metal La contributes to the formation of more easy reduction metal species, while the rare earth metal La as a structural aid, can also improve the dispersion of active components on the carrier. The large area of hydrogen reduction peak near 600°C of the Ni-W-E catalyst indicates that the Ni-W-E catalyst contains more WTO_3 of octahedral coordinated multinucleated polytungstic acid, indicating that the addition of EDTA facilitates the conversion of the tetrahedral tungsten species to the octahedral tungsten species.

The high temperature reduction peak of the tungsten species than the Ni-W catalyst moved significantly toward the low temperature, indicating that the chelating agent EDTA can effectively

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improve the sulfation of the metal, reduce the sulfide temperature, and improve the interaction between the active component and the composite carrier.

The area of the low-temperature reduction peak and the mixed phase reduction peak of the catalyst is further increased, indicating that the synergistic action of La and EDTA can promote the formation of more Ni-W-S active phases, so as to effectively improve the hydrodesulfurization activity of the catalyst.

3.3. BET

Table 1 shows the structural properties of the different catalysts. As can be seen from Table 1, the prepared Ni-W catalyst has a large specific surface area, which is consistent with the results reported in the literature [14]. The specific surface area of Ni-W-La catalyst was 251 $m^2 \cdot g^1$, an increase of 5.46%, indicating that the presence of La additives significantly increased the specific surface area of the catalyst, which facilitates the dispersion of Ni and W, increases the contact area, and provides a large amount for the catalytic reaction place. Compared to Ni-W, Ni-W-La catalyst, Ni-W-Both the E and Ni-W-La-E catalysts have relatively large specific surface areas, which are accompanied by increased pore size and decreased pore size. This may be because the chelation between the chelator and the metal ions effectively avoids the aggregation of active metals in the pore, but causes the blockage of part of the pore.

Table 1 Textural properties of different catalysts

catalytic agent	Specific surface area / $m^2\ g^{-1}$	Kong rong /$cm^3 \cdot g^{-1}$	aperture /nm
Ni-W	238	0.68	11.93
Ni-W-La	251	0.76	13.11
Ni-W-E	274	0.88	10.28
Ni-W-La-E	283	0.93	10.93

3.4. SEM

Figure 3 shows the SEM photos of the different catalysts. As can be seen from Figure 3, the grain diameter of Ni-W catalyst is larger and serious, and the catalyst of Ni-W on the carrier is significantly smaller than Ni-W, and more dispersed, which is consistent with the XRD results, indicating that the auxiliary La helps to reduce the granularity of the metal crystal, increase the dispersion of active components, more conducive to the Ni and W load on the carrier, and avoid sintering and clustering in the roasting process. Similar to Ni-W-La catalysts, the surface of Ni-W-E and Ni-W-La-E catalysts is relatively regular, and the active components are evenly dispersed, and basically no large particles accumulate, indicating that the addition of an appropriate amount of chelator is beneficial to the dispersion of the active components on the surface of the catalyst [15]

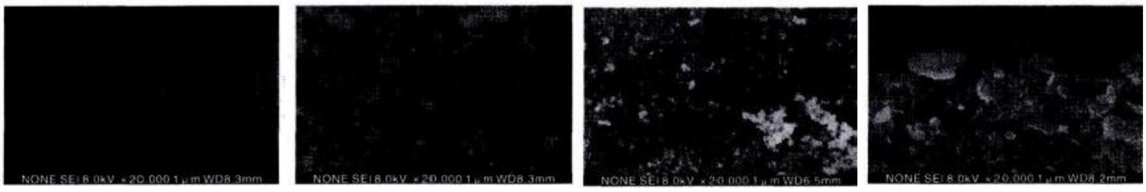

Figure 3 SEM images of different catalysts

3.5. Hydrogenation and hydrodesulfurization performance of the catalyst

Table 2 shows the reaction performance of thiophene hydrodesulfurization on different catalysts.As can be seen from Table 2, the removal rate of thiophene was higher on each modified catalyst than that of Ni-W catalyst, indicating that both La and EDTA have an important influence on the hydrodesulfurization activity of the catalyst. The thiophene conversion rate on Ni-W-La catalyst increased from 87.3% to 92.6%, and on Ni-W-E catalyst modified by EDTA to 95.1%, which increased by 5.3 and 7.8 percentage points relative to the unmodified Ni-W catalyst, respectively. The thiophene conversion rate of Ni-W-La-

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E catalysts simultaneously modified by La and EDTA was higher than that of La and EDTA alone, and the thiophene conversion rate was 99.7%, up 12.4 percentage points over the Ni-W catalyst.

Table 2 Activity of different catalysts forthiophene HDS

catalytic agent	w(La_2O_3) /%	n(EDTA): n(Ni)	Thiophene removal rate /%
Ni -W	0	0	87.3
Ni-W-La	2	0	92.6
Ni-W-E	0	1	95.1
Ni-W-La-E	2	1	99.7

4. The conclusion

The hydrodesulfurization catalyst with TiO_2-Al_2O_3 as the carrier and Ni and W as the active metal components was prepared, and the modification of rare earth metals La and EDTA and the modification of La-EDTA combination on the catalyst structure and hydrodesulfurization performance were investigated. La modification increases the specific surface area of TiO_2-Al_2O_3 composite carrier, improves the interaction between the carrier and the metal, effectively improves the metal sulfide, thus facilitates the formation of type Ni-W-S active phase, and the introduction of EDTA is conducive to the increase of pore capacity, promotes the conversion of tungsten species to more active octahedra, and forms more active phases to highly disperse the active metal on the composite carrier.

In the evaluation of catalyst hydrodesulfurization activity, three modified catalysts of thiophene sulfur removal rate reached more than 90%, among them, the La-EDTA combination modified catalyst thiophene conversion rate of 99.7%, not modified the conversion of catalyst hydrodesulfurization by 12.4%, showed higher hydrodesulfurization performance, the basic realization of complete removal of thiophene sulfur.

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