The mechanism of additives to unsupported Ni-Mo hydrodesulphurization catalyst

Shi Yan*, Su Feiming, Wang Xiaoqiang, Yao zhiwei, Liu jiaming

1Chemical Industry and Environment Department of Petrochemical College, Liaoning University of petroleum chemical industry, Fushun, Liaoning, 113001, China

*Corresponding author’s e-mail: shiyan1816@163.com

Abstract. A series of highly active unsupported Ni-Mo hydrodesulphurization catalyst prepared by coprecipitation method and characterized effect of additives Al2O3 on the structure performance by BET, and Py-IR tests. The results indicated the additives Al2O3 greatly increased the pore diameter and specific surface area and mechanical strength. And it increased the acid of L acid while formatted B acid sites. This paper also characterized the influence of phosphorus to the Ni-Mo catalyst. BET results show that phosphorus blocked the catalyst pore structure, specifically reduced the surface area of the Ni-Mo. But TPR, FT-IR studies have shown that phosphorus can form Al-P-O structure, weaken interaction between active phase and Al2O3, while the amount of tetrahedral Mo species was decreased and octahedral Mo species was increased.

1. Introduction

As for the active ingredient and site density are much higher than the conventional supported catalysts, unsupported catalysts have the very high capacity of hydrogenation desulfurization denitrogenation and aromatics saturation in the processing of crude oil[1]. Since 2011, when a series of NEBULA unsupported hydorefining catalyst successfully industrialization for the first time, people began to concern about it. As the studies shown, the activity of the unsupported catalysts is at least three times of supported hydrotreating catalysts[2-3]. Currently unsupported catalyst mainly regards VIB, VIII metals as the active phase in which the Ni-Mo catalyst has a pretty high hydrodesulfurization performance, and it can be ultra-deep desulfurization for high-sulfur diesel fuel[4].

Aldridge CL, who found that Al2O3 can significantly improve the specific surface area, pore volume, pore diameter and mechanical strength[5]. It is because that Al2O3 has regular mesoporous structure, good pore size distribution, large pore volume and surface area[6]. What’s more, it has strong Lewis acidity. Phosphorus is the second auxiliaries of unsupported catalyst which is commonly used in hydrodesulphurization[7]. However, Roquero P and others believe that the functional mechanism of phosphorus is that the P promote the tetrahedral Mo shift to octahedral[8]. Besides, the octahedral Mo is able to be vulcanized, and is the precursor of forming highly reactive type II Ni-Mo-S active phase, which contribute to improve HDS activity[9]. Some researchers Sigurdson S think a moderate amount of phosphorus can change the catalyst’s pore structure, improve the dispersity between the edge active component, and increase the activity of HDS and HDN. This paper studied the additive Al2O3 and phosphorus on the impact of unsupported catalyst structure of Ni-Mo[10].
2. Experiment

2.1. Reagents and materials
Nickel nitrate (Ni (NO\(_3\)) \(_2\) 6H\(_2\)O, AR.), Ammonium molybdate ((NH\(_4\)) \(_6\)Mo\(_7\)O\(_4\)H\(_2\)O, AR.), Aluminum sulfate (Al\(_2\)(SO\(_4\))\(_3\) 18H\(_2\)O AR.), Ammonium dihydrogen phosphate (NH\(_4\)H\(_2\)PO\(_4\), AR.), Ammonia (NH\(_3\)H\(_2\)O, AR.), Ethanol (C\(_2\)H\(_5\)OH, AR.) \[^{[1]}\].

2.2. Catalyst Characterization

2.2.1. Analysis of N\(_2\) adsorption (BET method)
Using the Micromeritics TriStar 3000 automatic adsorption instrument, samples were analyzed for surface area, pore volume and pore diameter. The catalyst was vacuum degassed at 300 °C 6.0h, then backfilled with nitrogen at -196 °C to normal pressure.

2.2.2. Raman spectroscopy (LRS)
Raman analysis of experimental production company in HoRiBAloBiN Yvon LabRAM. HR800 type were analyzed on a confocal Raman microscope, The excitation light source of monochromatic laser 325nm , slit 400nm, the signal integration time 10-20s, 50 times as long as the lens focal length, the input laser power 100mW.

2.2.3. Infrared spectroscopy (FT-IR, Py-IR)
IR spectrum of the catalyst sample measurement sample mainly acid type. During the experiment using NicoLET 6700 type FI-IR analyzer, After the catalyst sample was dehydrated at 300 °C 2h, cooled to room temperature and pyridine adsorption treatment, vacuum treatment at 140 °C2h, pyridine adsorbed on the catalyst sample peak measured to obtain an acid type.
Py-IR was measured using the Nicolet-58SXC type FI-IR analyzer. Samples were dehydrated at 300 °C conditions 2h, cooled to room temperature adsorption of pyridine, treated at 140 °C evacuated 2 h, pyridine adsorption peaks on the sample measured by infrared spectroscopy, thereby determining the type of acid sample \[^{[12]}\].

2.3. Preparation of catalyst
Coprecipitation unsupported Ni-Mo catalysts:
The aluminum sulfate is dissolved in the three-necked flask, and added to aqueous ammonia to adjust the pH value at the same added to dissolved ammonium molybdate solution, and heated to a certain temperature, obtained solution a\[^{[13]}\]. Nickel nitrate dissolved in water and the solution was heated to a same temperature to obtain solution b. The b solution was slowly added drop wise to a solution of a, and reaction for 3 hours. Filtered while hot, washed, and dried to obtain a catalyst precursor referred to as A\(_2\), the Ni-Mo catalyst referred as A\(_1\)\[^{[14]}\]. Preparation of a certain concentration of ammonium dehydrogen phosphate solution, impregnated into the catalyst precursor in the mass fraction of phosphorus catalyst mass accounted for 1.5%, then the prepared precursor was dried and calcined, obtained a unsupported Ni-Mo-P-Al\(_2\)O\(_3\) catalyst denoted as B\(_2\)\[^{[15]}\].
3. Results and Characterization

![Graph showing pore size distribution and pore structure of Ni-Mo catalyst.](image)

Figure 1. Pore size distribution and pore structure of Ni-Mo catalyst.

As can be seen from Figure 1, the addition of additives Al₂O₃ significantly change the pore size distribution and pore structure. Ni-Mo catalyst has the hole concentrated in 1.5-2.0nm and 2.5-3.0nm, may be the active has been ingredient diffused. Ammonium molybdate and nickel ammonium nickel molybdate ammonium formed a support structure rearrangements during calcining. After adding Al₂O₃, pore size distributed between 3.5-4.5nm, and no other channel, may be due to the addition of organic improved the catalyst specific surface area and pore volume, and then expand the diameter. And Al₂O₃ itself has a supporting structure, for the catalyst provides greater diameter[16]. This structure dissolve macromolecules nitrides, sulfides, and aromatic compounds, thereby improving denitrification, desulfurization and dearomatization activity of the catalyst.

|            | Catalyst surface area (m²/g) | Pore volume (mL/g) | Pore diameter (nm) | Mechanical strength (N/nm) |
|------------|------------------------------|-------------------|-------------------|----------------------------|
| A₁         | 73                           | 0.18              | 3.6               | 8.7                        |
| A₂         | 189                          | 0.67              | 4.5               | 18.9                       |

Table 1 showed Ni-Mo catalyst surface area is only 73 m²/g, pore volume is 0.18 mL/g, pore diameter is 3.6nm, and the mechanical strength only has 8.7N/nm; and Ni-Mo-Al₂O₃ surface up to 189 m²/g, pore volume is 0.67mL/g, pore diameter is 4.5nm, and the mechanical strength is 18.9N/nm. The catalyst surface area and pore volume almost doubled after adding Al₂O₃. And mechanical strength increased significantly. Al₂O₃ can effectively expand the pore structure and it is a good additive[17].
Figure 2. Ni-Mo-Al$_2$O$_3$ Catalysts adsorption line.

Figure 2 show that Ni-Mo-Al$_2$O$_3$ adsorption line belong to IUPAC classification of H$_4$ type, should be slit channels$^{[18]}$. Hysteresis loop mainly distributed at pressure in the 0.5 to 0.9, indicating that the catalyst formatted a large number of big hole and the hysteresis loop a significantly wider than the reference agent after adding Al$_2$O$_3$, this further illustrate the function of Al$_2$O$_3$.

3.1. Py-IR analysis

Figure 3 is pyridine adsorption and desorption spectrum in 250 °C. Generally believed absorption peak at 1450 cm$^{-1}$ and L is an acid after the pyridine ligand role in the formation Py-L, C-C (N) bond stretching vibration generated by this peak characterization L acid sites; 1488 cm$^{-1}$ absorption peak at

| Catalysts | Total Acidic (mmol/L) | B acidic (mmol/L) | L acidic (mmol/L) |
|-----------|-----------------------|-------------------|-------------------|
| Al$_2$O$_3$ | 0.117 | 0 | 0.117 |
| A$_1$ | 0.252 | 0 | 0.252 |
| A$_2$ | 0.355 | 0.053 | 0.302 |

Figure 3 is pyridine adsorption and desorption spectrum in 250 °C. Generally believed absorption peak at 1450 cm$^{-1}$ and L is an acid after the pyridine ligand role in the formation Py-L, C-C (N) bond stretching vibration generated by this peak characterization L acid sites; 1488 cm$^{-1}$ absorption peak at
common after absorption by B acid and L acid and pyridine role. After the 1540 cm$^{-1}$ a weak absorption peak near, by the action of pyridine with a protic acid formed protonated PyH$^+$, CC (N) bond stretching vibration generated acid site characterization B$^{[19]}$.

The figure shows the reference agent Ni-Mo and Ni-Mo-Al$_2$O$_3$ catalyst spectra are almost identical, indicating added acidic have no change in the surface of Al$_2$O$_3$ in Ni-Mo catalysts, because Al$_2$O$_3$ acid itself have no B, only a small amount of L acid. This may be wrapped in Ni-Mo composite, not in the surface of the catalyst. A$_1$ can be seen from Table 2, the catalyst only have 0.025 mmol/L acid L, no B acid. But after adding Al$_2$O$_3$ L acid increased, while generating the B acid, increasing the total amount of acid$^{[20]}$. Usually the main B acid are provided by the metal Ni, L acid are provided by metal Mo, but B acid and L has increased after adding Al$_2$O$_3$, this is because Al$_2$O$_3$ promote the interaction between Ni-Mo, Ni with Mo-O-Ni way to increase the amount of L acid and the produced B acid sites.

### 3.2 Effect of phosphorus on the catalyst structure

![Figure 4. Catalysts performance which after impregnating phosphorus.](image)

**Table 3. BET Analysis Results**

| Catalyst | Surface area (m$^2$/g) | Pore volume (mL/g) | Pore diameter (nm) |
|----------|------------------------|--------------------|--------------------|
| A$_2$    | 189                    | 0.67               | 4.5                |
| B$_2$    | 131                    | 0.18               | 5.2                |

As can be seen from Table 3 and Figure 4, after impregnating phosphorus, catalyst specific surface area becomes 131 m$^2$/g, pore volume become 0.18 mL/g, pore diameter is 5.2 nm. Visible after impregnating phosphorus significantly reduce surface area and pore volume, because the secondary pore was blocked for adding phosphorus, thereby reducing the pore volume. But the most probable pore size has increased after dipping phosphorus, may be due to the addition holes will be corroded, making the holes bigger, and make the pore size probably increased$^{[21]}$. 
H$_2$-TPR curve can provide information about the oxidation state of the catalyst for reducing the interaction between the different components\cite{22}. Figure 5 is a H$_2$-TPR curve of Ni-Mo catalyst in oxidation state. Generally MoO$_3$ reduction has two steps: MoO$_3$ to MoO$_2$ and then reduced to Mo. TPR reduction peak at low temperature is the tetrahedral Mo convert to octahedral (Mo$^{6+}$-Mo$^{4+}$). These Mo is an amorphous, high defect multilayer molybdenum oxide or heteropoly acid, and the octahedral Mo is highly active primary precursor in hydrodesulphurization catalyst\cite{24}. The high-temperature reduction peak mainly tetrahedral M reduction, these reduction are highly dispersed Mo and Mo oxide MoO$_3$, but tetrahedral Mo species difficult to convert into a highly active Ni-Mo-S phase activity. In the same conditions HDS activity have concern about reduction temperature, in the lower the reduction temperature, catalyst are more vulcanization, and have the better HDS activity.

From TPR we can see, Ni-Mo catalyst have 3 reduction peak appears in the range of 300-800°C, respectively, at 430 °C, about 550 °C and 700 °C. Where the apparent hydrogen consumption peak at 430 °C, which corresponds to the low valence state reduction of Mo and Ni reduction. In more moderate reduction peak of 550-650 °C, attributed to the interaction of species Ni-Mo-O reduction. Low valence state Mo reduction peak at 750 °C. High temperature reduction peak at 700-750 °C is NiAlO that the Ni and Al$_2$O$_3$ formed. Mo reduction peak area becomes larger after joining P. The peak of low valence state Mo was reduced at high temperature, indicating that after joining P, tetrahedral Mo species reduce and octahedral Mo$^{6+}$ species increased. Such structure is conducive to increase high activity Ni-Mo-S phase.

At the same time, peak of 700-750 °C disappeared. This is due to the AlPO$_4$ phase that P and Al$_2$O$_3$ formatted, and reduce the interaction between the active component Ni and Al$_2$O$_3$. On the other hand, after dipping P temperature increase about 30°C at low temperature, this is because P increases the hole diameter, particles and the reduction temperature as the BET analysis\cite{23}.

### 3.3. IR analysis

It can be seen from Fig. 6, the Ni-Mo-Al$_2$O$_3$ catalyst appears as a large peak at 3735-3688 cm$^{-1}$, which is the formation of hydroxyl vibration, -OH and Al to form Al-OH and Al-OH-Al bonds cover in the Al$_2$O$_3$ which is not conducive to the formation of active sites 3440 cm$^{-1}$ vibration peak is a crystal water. In 1640 cm$^{-1}$ peak is stretching vibration of N-H-N, indicate that there has a small amount of ammonium that was decomposition. The fingerprint region of 1000-600 cm$^{-1}$ is stretching vibration of molybdate. The vibrational wavenumbers of Mo=O at 1050-900 cm$^{-1}$. The vibration peak of Mo
vibrational wavenumbers of Mo=O at 1050-900cm⁻¹. The vibration peak of Mo oxide at 935 cm⁻¹ and 848 cm⁻¹. 800-700cm⁻¹ is the Mo-O-Mo vibration or O-Mo-O stretching vibration, or the both The B₂ catalyst at the 3735-3688cm⁻¹ peak weak even disappeared. This indicate Al-OH-Al and Al-OH bond wreaked after impregnate P. This is because the addition of P formatted P-OH bond and formatted more -OH in the catalyst and there are more activity Mo This activity will increase the activity of HDS[21] At the same time after impregnating P Mo oxide peak from881cm⁻¹ change to 850 cm⁻¹ and the peak strength increased Further showed that formatted Mo activity species after addition of phosphorus[24].

3.4. Raman analysis

Raman spectroscopy for the analysis of interactions between metal and non-metallic element groups, and commonly used in the fingerprint region (wave number is less than 1000 cm⁻¹) identification of...
vibration peaks make up deficiencies in the infrared region. This paper focuses on the distribution of Mo in the fingerprint region. Figure 7 shows, for the Ni-Mo-Al2O3 catalyst Raman fingerprint region have four main peaks at 300-410 cm\(^{-1}\), 520-600 cm\(^{-1}\), 700-900 cm\(^{-1}\), 900-950 cm\(^{-1}\). In the 300-410 cm\(^{-1}\) mainly has two peaks, one focused on about 350 cm\(^{-1}\), is the V\(_3\) stretching vibration of Mo tetrahedral structure. It is Mo-O of MoO\(_4\) structure another is mainly Mo octahedral at 370 cm\(^{-1}\), peaks at 579 cm\(^{-1}\), attributed to the active ingredient with Al-O stretching vibration, it is Al-O bond vibration. of Mo-O-Al. Third most broad peak at 800-900 cm\(^{-1}\). The Mo-O-Mo structure of tetrahedral Mo vibrational in the peak of 880 cm\(^{-1}\). This shows that mainly is tetrahedral Mo the catalyst A\(_2\).

After addition of P, the peak shape is almost no change, but the peak of 800-900 cm\(^{-1}\) blue shift. 880 cm\(^{-1}\) of the peak area is reduced, increasing the peak area of 960 cm\(^{-1}\) and the And the peak 960 cm\(^{-1}\) is octahedral Mo V\(_3\) of the bending vibration molybdate formed Mo\(_7\)O\(_{24}\)\(^{6-}\) stretching vibration of the Mo = O. Indicate the amount of tetrahedral Mo species was decreased and octahedral Mo species was increased after adding phosphorus There was no peak at 800 cm\(^{-1}\) indicating that the compound is not formed MoO\(_3\), while Mo octahedral structure also shows that Mo species uniformly distributed At 700 cm\(^{-1}\) peak have a marked concave, indicate Ni is not formed, and immersed dispersion better.in Mo skeleton. After joining P at the peak of 564 cm\(^{-1}\) broadening slightly, indicating that the active metal and Al2O3 weakened, it is easy to form octahedral Mo species. Comprehensive TPR analysis, the Raman spectrum further reduces the number of tetrahedral Mo species, increasing the number of octahedral Mo species; reduces the formation of MoO\(_3\). Increased dispersible of Mo and Ni\(_2\).[25]

4. Conclusion
The additives Al\(_2\)O\(_3\) greatly increased the pore diameter and specific surface area and mechanical strength. High specific surface area and pore volume and acid, is a prerequisite for high activity catalyst. And it increased the acid of L acid while formatted B acid sites The Ni-Mo-Al2O3 catalyst prepared by coprecipitation phosphorus blocked the catalyst pore structure, specifically reduced the surface area of the Ni-Mo. But phosphorus can form Al-P-O structure, weaken interaction between active phase and Al2O3, while the amount of tetrahedral Mo species was decreased and octahedral Mo species was increased. And the octahedral Mo species are believed to improve high activity II type Ni-Mo-S phase in the catalyst, and improve HDS and HDN activity.

Acknowledgements
National Natural Science Foundation Project of China, Project No.: 21978125
Liaoning natural foundation project, Project No.: 20170520251
Liaoning Provincial Department of education project, Project No.: L2019002, L2017LFW008

Reference
[1] Plantenga F.L., Cefortnain R., Eusbouts S., Hoitert F., Anderson G.H., Miseo S, Soled S., Riley K., Fujita K., Inouey Nebula. (2003) A hydroprocessing catalysts with breakthrough activity. J. Stud Surf Sci Catal, 145 (8): 407–410.
[2] Li He, Yin Changlong, Zhao Leiyan, Wang Xiao, Liu Yunqi, Liu Chenguang. (2003) Research progress of non-supported hydrotreating catalyst. J. Petroleum Chemical 42 (7): 811–817.
[3] Soled S.L., Miseo S., Zhiguo H.. Bulk Ni-Mo-W catalysts made from precursors containing an organic agent: US, 7544632 P. 2009-06-09.
[4] Mayo S., Brevoord E, Plantenga F, et al. NebulaTM catalyst provides proven economic returns [C/CD]. NPRA Annual Meeting, AM-05-14. San Francisco, 2005.
[5] Eijsbouts S., Mayo W., Fujita K. (2007) Unsupported transition metal sulfide catalysts: From fundamentals to industrial application. J. Applied Catalysis A: General 322: 58–66.
[6] Liu Huan, Yin Changlong, Zhao Leiyan, Liu Chenguang. (2013) Hydrothermal synthesis of Ni-Mo catalyst and its catalytic hydrogenation performance. J. Petroleum Refining and Chemical 44 (9): 19–23.
[7] Kraush P. R. (1997) The effect of phosphorus on oxidic Ni-Mo (CoMo) /Al₂O₃ catalysts: A solid state NMR investigation. J. Catalyst 170 (1): 20–28.
[8] Zhou Tongna, Yin hailiang, Han Shuna, Chai Yongming, Liu Yunqi, Liu Chenguang. (2009) Effect of different phosphorus content on NiMoPAI₂O₃ hydrotreating catalyst. J. of fuel chemistry 37 (3): 330–334.
[9] Alonso G., Espino J., Berhault G., Avarez L., Rico J.L. (2004) Hydrotreating catalyst J. Application Catalyst A 26(2): 29-40.
[10] Heirem J.M., Reyes J., Roquero P.et al. (2005) New hydrotreating Ni-Mo catalysts supported on MCM₄₁ modified with phosphorus J. Microporous Mesoporous Mater 83 (1): 283–291.
[11] Zhu Manzhou, Zhu Xifeng, Guo Qingxiang et.al. (2006) Characteristics of biomass pyrolysis oil from corn stalk. J. Journal of China University of science and technology 36(4): 374–377.
[12] G.J. An, Y.Q. Liu, et al., (2007) Prog. chem. J. 19 (2): 243–249.
[13] Rajagopal S., Marini H.J., Marzari J.A., Miranda R., (1994) J. Catalysts 147 (1): 417.
[14] Hu Dawei, Yang Qinghe, Sun Shuling,et.al. (2011) Effect of phosphorus on the performance and active structure of Mo-W catalyst. J. Petroleum Refining and Chemical 42(5): 1–4.
[15] Sigurdsen S, Sadam M.V., Dalai A.K,et al. (2008) Phosphorus promoted metallic NiMoW/Al₂O₃ sulfide catalysts in gas oil hydrotreating. J. Catalyst A Chem 29 (1): 30–37.
[16] Kasztelan S., Toulhoath J., Bonnelle J.P. (1984) A geometrical model of the active phase of hydrotreating catalysts. J. Appl Catal. 13 (1): 127–159.
[17] Sun Yanyao, Li Fengyan, Li Qingjie, (2008) Effect of phosphorus content on the performance of supported molybdenite catalysts J. Petroleum Refining and Chemical 39 (8): 46–49.
[18] Qian E.W., Abe S., Kurahashi T., Kagawa Y., Ikeda H. (2011) Prep ACS Div. J. Petroleum Chem 56 (2): 99.
[19] Olivas A., Galván D.H., Alonso G., Fuentes S., (2009) J. Application Catalysts A 352 (1): 10-16.
[20] Nikolova D., Edreva-Kardjieva R., Giurginca R., Meghea A., Vacros A., Voiyatizis G.A.(2007) Chemical Kordulis J. Vibr. Spectr. 44: 343.
[21] Ma X.L., Sakanishi K., Mochida I. (1994) Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel J. Industrial Engineering Chemistry Research 33(2): 218–222.
[22] L.G.A. Van De Water, Bergwerff J.A., Nijhuis T.A., Dejong J.P., Weckhuysen B.M. (2005) J. JACS 127: 5024.
[23] Beyhan E., Sezer E., Ramis M.O., Alime C. (2013) High-surface-area SBA-15–SO₃H with enhanced catalytic activity by the addition of poly (ethylene glycol) J. Journal of Porous Materials, 20 (5): 1041–1049.
[24] Vakros J., Bourikas K., Kordulis C., Lycourghiotis A. (2003) J. Phys. Chem. B107: 1804–1808.
[25] Qian W., Yamada S., Ishihara A, Ichinoseki M., Kabe T. (2001) J. Sekkiyu Gakkashi, 44(4): 225-229.