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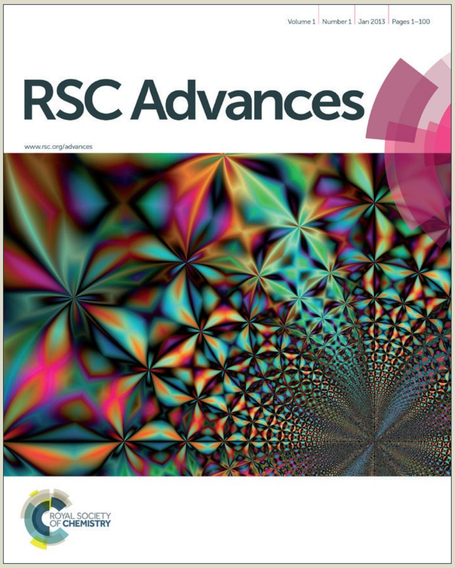

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ARTICLE

Effect of promoter on the HDS activity of alumina-supported Co-Mo sulfide catalysts

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Xilong Wang[1], He Fang[1,2†], Zhen Zhao[1], Aijun Duan[1]*, Chunming Xu[1]*, Zhentao Chen[1], Minghui Zhang[1], Peng Du[1], Shaotong Song[1], Peng Zheng[1], Kebin Chi[3]

A series of CoMo/δ-Al_2O_3 catalysts promoted by different organic and inorganic cobalt salts were successfully prepared using low-cost δ-Al_2O_3 as supports through a two-step incipient-wetness impregnation method. The obtained catalysts were indicated as MoCo-N/δ、MoCo-S/δ、MoCo-A/δ and MoCo-D/δ, in which N, S, A, D, and δ represent cobalt nitrate, cobalt sulfate, cobalt acetate, cobalt diacetylmethane, and δ-Al_2O_3, respectively. The as-synthesized catalysts were introduced to the hydrodesulfurization (HDS) process of fluid catalytic cracking (FCC) diesel, in a fixed-bed reactor. The oxidized catalysts and the corresponding sulfurized catalysts for HDS were characterized by UV-Vis, Raman, X-ray diffraction, TPR, and XPS techniques. The catalytic activities followed the order of MoCo-A/δ < MoCo-N/δ < MoCo-D/δ < MoCo-S/δ. These catalytic results could be ascribed to the introduction of different cobalt salts decreasing the metal-support interaction(MSI), and led to the formation of easily reduced Mo species, which were the precursors to form more active sites that could enhance HDS activity of the catalysts. The highest activity shown by the catalyst of MoCo-S/δ could be ascribed to its (1) higher metal dispersion, (2) lower Mo reduction temperature, and (3) higher sulfurization degree. As a result, the excellent catalytic performance could be attributed to its outstanding promoter effect.

1. Introduction

The development of highly active hydrodesulfurization (HDS) catalysts has been one of the principal issues in the petroleum industry to meet the ever increasing stringent environmental regulations. [1,2] Mo or W sulfide catalysts promoted by Co or Ni on alumina are widely used in HDS processes due to their high selectivity and activity.[3,4] It is generally believed that the active phase of Co-Mo HDS catalysts is so-called "CoMoS" phase, in which Co atoms are located on the edge of MoS_2 particles.[5] During the preparation the individual sulfide species like Co_9S_8 are formed, leading to a loss of promoter to the detriment of the active phase,[6,7] which prevents the promoter incorporated into the active phase and thus decreases the reactivity. A better control of the location of the promoter could be obtained by introducing the promoter metal onto MoS_2/support to get the supported promoted phase, as proposed by several research groups.[8,9]

In recent years, the configuration of active phases and the promotion effect of Co/Ni on the supported or bulk Mo sulfides evoke the attention of researchers in improving HDS performance of the catalysts. Candia et al.[10,11] revealed that the sulfidation of MoS_2 particles decreased the interactions between MoS_2 particles and the support material, leading to the formation of type II CoMoS phase. Moreover, they found that HDS reactivity was linearly correlated to the amount of CoMoS phase. [12, 13] The formation of the Co-Mo sulfide species explained the generation of strong catalytic synergies between Co and Mo. Some research groups have reported the main focuses, including the Co or Ni promoters,[14,15] their roles in modifying active nanoparticle morphologies, and the active site performance. [16] Schweiger et al. [17] reported that for Mo-edge fully promoted by Co at high chemical potential, Co was situated on both edges with 100% sulfur coverage while S-edge with 50% sulfur coverage and the Co atoms on the Mo-edge were energetically less favorable. Bezverkhyy et al. [18] used cobalt acetylacetonate as Co precursor to promote molybdenum sulfide supported on alumina, and found that the solids could be directly used as catalyst without resulfidation. They also proved

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1 State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, P. R. China;
2 Yunnan Yuntianhua Petrochemical Co., Ltd.,Yunnan, 650300, P.R. China;
3 Petrochemical Research Institute, PetroChina Company Limited, Beijing 100195, P. R. China;

[†] This author has equal contribution as the first author

*Aijun Duan: Email: duanaijun@cup.edu.cn; Tel: 86-10-89732290
*Chunming Xu: xcm@cup.edu.cn; Tel: 86-10-89733392

that the use of $Co(NO_3)_2$•$6H_2O$ as Co source led to a weaker synergetic effect. Okamoto et al.[19,20] found that CoMoS phases were selectively formed by use of $Co(CO)_3NO$ as a precursor in which the Mo content was fixed approximately at a monolayer loading. Gandubert et al. [21] used X-ray photoelectron spectroscopy (XPS) in conjunction with DFT, suggesting that Co-Mo mixed sites on the Mo-edge were active for the hydrogenation of toluene, while the S-edge fully promoted by Co showed a lower activity.

Many studies have shown that the hydrogenation activity of MoO_3/Al_2O_3 could be dramatically improved by the introduction of Co, and the bimetallic synergy was helpful for the generation of highly active CoMoS phase. The cobalt nitrate is generally used in the traditional CoMo catalyst. It is reported that different cobalt sources had great influence on the activities of catalysts. However, the effect of different cobalt salts on the HDS activity of catalysts was rarely reported and lack of systematic research.

In this work, firstly, δ-Al_2O_3 was used as the support material and the supported CoMo catalysts promoted by different organic and inorganic cobalt salts were synthesized by incipient-wetness impregnation method. Secondly, a series of supported CoMo catalysts for HDS were characterized by UV-Vis, Raman, XRD, TPR, and XPS techniques. Finally, the effect of different organic and inorganic cobalt salts on the FCC diesel HDS activity was investigated to obtain the catalyst with the best performance.

2. Experimental

2.1 Preparation of the catalyst

The δ-Al_2O_3 was prepared by calcination of the hydrated boehmite, bought from Zhengzhou Aluminum Industry Research Institute, in air at 1173 K for 5 h with the heating rate of 2 K min^{-1}. Active metal components of Mo and Co were stepwise loaded on the δ-Al_2O_3 supports via a two-step incipient wetness method impregnated with aqueous solutions of heptamolybdate tetrahydrate (($(NH_4)_6Mo_7O_{24}$•$4H_2O$, Sinopharm Chemical Reagent, 99.0wt%) and cobalt salts. The details of the preparation were shown as follows:

A certain amount of ammonium molybdate was dissolved in deionized water and then Al_2O_3 was added into the solution. After impregnation, the samples were dispersed by ultrasonic for 15 min, dehydrated at 110℃ for 2 h and calcinated at 550℃ for 6 h to obtain a series of Mo/supporters. Cobalt salts were introduced by incipient-wetness impregnation method according to the solubility, the details were as follows:

A certain amount of cobalt salts were dissolved in certain solvents and Mo/supporter catalyst was added in. Then the samples were dispersed by ultrasonic for 20 min, dehydrated at 110℃ for 2 h and calcinated at 550℃ for 6 h to obtain a series of CoMo supported catalysts. The obtained catalyst was squashed and broken into particles with 40-60 mesh.

For dissolving different cobalt species, including cobalt nitrate (Sinopharm Chemical Reagent, 98.5wt%), cobalt sulfate (Tianjin Guangfu Fine Chemical Research Institute, 99.5wt%) and cobalt acetate (Sinopharm Chemical Reagent, 99.5wt%), deionized water was used as solvent. For impregnating cobalt diacetylmethane (Sinopharm Chemical Reagent, 99.0wt%), methanol was used as solvent. The obtained catalysts were indicated as MoCo-N/δ、MoCo-S/δ、MoCo-A/δ and MoCo-D/δ, in which N, S, A, D, and δ represent cobalt nitrate, cobalt sulfate, cobalt acetate, cobalt diacetylmethane, and δ-Al_2O_3, respectively. The metal compositions of the catalysts were 12 wt.% of MoO_3 and 3 wt.% of CoO.

2.2 Characterization of the catalysts

The wide–angle ($2\theta = 5.0$–80.0^{o}) X–ray diffraction patterns were determined on a Rigaku RINT D/Max-2500 powder diffraction system, using the Cu Kα radiation at 40 kV and 50 mA. The UV–Vis diffuse reflectance spectra of the catalysts were recorded using a UV–Vis spectrophotometer (Hitachi U-4100). The powder catalysts were characterized in the 200–800 nm range at room temperature. H_2–TPR experiments of the catalysts were performed on a Quantachrome apparatus (Auto-sorb-iQ, USA) in a 10% H_2/Ar flow at 40 ml/min. The Raman spectra for the catalysts were recorded on a Raman microscope (Spectra-Physics model 163), operated at the laser wavelength of 532 nm. X–ray photoelectron spectroscopy (XPS) analyses of the sulfided catalysts were carried out in a Thermo Fisher K–Alpha spectrometer equipped with an analyser mode of CAE operating at a fixed pass energy of 40 ev and working under vacuum ($<10^{-9}$ mbar). All the data were acquired using Kα (hv = 1486.6 ev), and the binding energy were calibrated taking C 1s (BE = 284.6 ev) as an internal standard. Before analysis, the catalysts were freshly presulfided according to the same sulfidation procedure as the catalytic activity evaluation, and stored under cyclohexane to prevent oxidation.

2.3 Catalytic performance evaluation

The HDS activity tests were evaluated in a fixed-bed reactor ($D = 9$ mm, $L = 50$ cm) with 2 g (40-60 mesh) catalyst using Hohhot FCC diesel with the sulfur content of 1013.78 $\mu g\cdot ml^{-1}$ as feedstock. The weighted catalyst was presulfided with 2 wt% CS_2 in cyclohexane, 4.0 MPa, 593 K, H_2/cyclohexane ratio of 600 ml/ml and weight hourly space velocity (WHSV) of 1.0 h^{-1} for 4.0 h. After sulfidation, the HDS reactions were performed at 623 K, 5.0 MPa, 600 ml/ml and 1.0 h^{-1}. The liquid product was collected at steady state after 9 h on stream. The HDS activities (η) are calculated as $\eta = (S_f - S_p)/S_f$, where S_f refers to the content of sulphur in feed, and S_p refers to the content of sulphur in products. The sulfur contents were tested by a RPP-2000SN sulfur and nitrogen analyzer (Taizhou Central Instruments Co. Ltd. P.R. China), The test deviation of the sulfur analyzer is 1 $\mu g\cdot ml^{-1}$, therefore, the deviations of HDS efficiency are around 0.10%.

3. Results and discussion

3.1 Characterization of catalysts

3.1.1 XRD characterization of the oxide CoMo catalysts

Fig.1 shows the wide–angle XRD spectrogram of the catalysts with δ-Al_2O_3 as supporter and different cobalt salts as promoters. The intensity of characteristic peaks of δ-Al_2O_3（2θ=66.95°, 45.62°, 46.48° and 37.6°）decrease after the loading of active metals, and the characteristic peak at 2θ=26.8° belongs to β-$CoMoO_4$, as shown in Fig.1.[22] For different cobalt salts, the intensities of the characteristic peaks are different and increase as the following order: MoCo-S/δ < MoCo-D/δ < MoCo-N/δ < MoCo-A/δ, showing that the better dispersion of active metal of catalysts with sulfate as assistant additives. The existence of small amounts of β-$CoMoO_4$ promotes the synergies between Co and Mo, resulting in the formation of Co-Mo-S active phase after sulfidation.

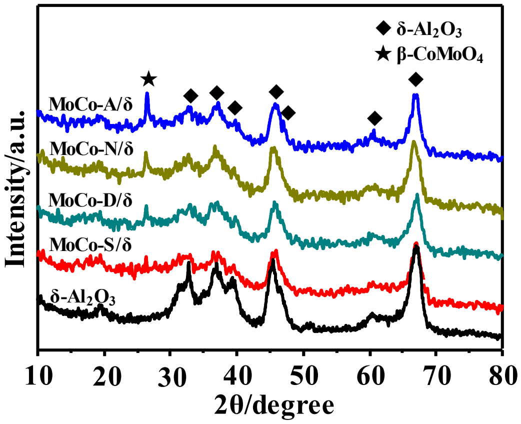

Fig. 1. XRD patterns of the series supports and catalysts with different cobalt salts.

3.1.2 UV-Vis spectra of the oxide CoMo catalysts

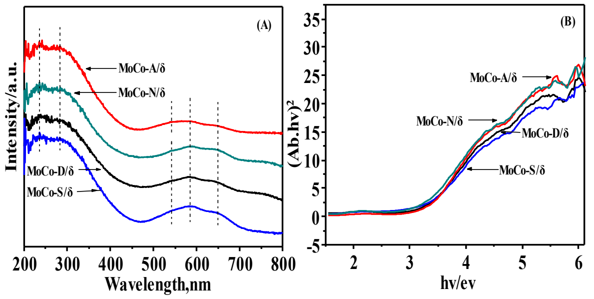

Fig. 2. (A) UV-vis DRS spectra, (B) plots of a 1/2 versus photon energy (hν) of MoCo/δ with different cobalt salts.

UV-vis DRS spectrum is usually applied to study the species of MoO in CoMo catalysts. Fig.2 shows the UV-Vis DRS spectra and photoelectron spectroscopy diagrams of MoCo/δ-Al_2O_3 catalysts with loading of different kinds of cobalt. Polymorphous crystalline aluminia based catalysts exhibit adsorption peak between 200-400 nm which belongs to Mo oxide. The adsorption peaks between 220-255 nm, 250-350 nm belong to tetrahedron coordination Mo(T) species and low polymetric octahedral coordination Mo(O) species, respectively.[23]

The as-prepared catalysts present three successive absorption peaks between 500-650 nm, which are ascribed to the tetrahedron coordination divalent Co species.[24] Besides, the adsorption peak of 590 nm belongs to the characteristic peak of β-$CoMoO_4$. The intensity of this adsorption peak increases as the following order: MoCo-S/δ < MoCo-D/δ < MoCo-N/δ < MoCo-A/δ, which is in accordance with the result of XRD characterization.

As shown in Fig.2 (B), the energy band gap decreases with the increase of the average particle size of molybdenum oxides in the catalysts. Besides, the energy band gaps of Mo species change with the introduction of different cobalt salts. When cobalt sulfide was used, the energy band gap of Mo species increased obviously, indicating that the average particle size of molybdenum oxides decreased and Mo species were distributed well in the catalysts.

3.1.3 H_2-TPR characterization of the oxide CoMo catalysts

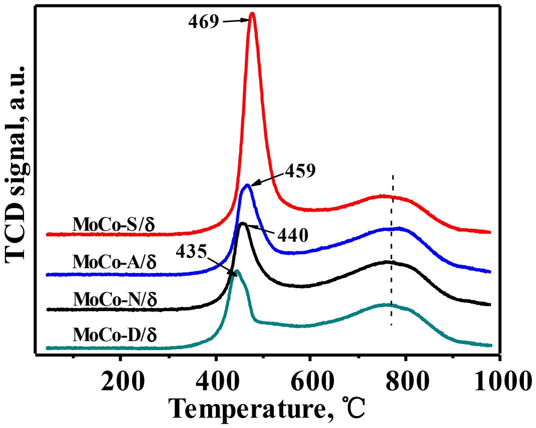

Fig. 3. H_2-TPR profiles of MoCo/δ-Al_2O_3 with different cobalt salts.

H_2-TPR is applied to study the interaction between MoCo species and the carrier by characterizing the reduction of MoCo species on the catalyst surface by H_2. Fig.3 displays the H_2-TPR profiles of MoCo/δ-Al_2O_3 with different cobalt salts.

The as-prepared catalysts showed two obvious reduction peaks of H_2 within the temperature range of 400–480 ℃ and 770–900 ℃, as shown in Fig.3. However, there were no apparent reduction peaks within the temperature scope of 600–630 ℃, which belong to the large MoO_3 particles. The first strong reduction peak is around 470 ℃, which is ascribed to the first step of Mo reduction ($Mo^{6+} \rightarrow HxMoO_3 \rightarrow Mo^{4+}$) of highly dispersed octahedral coordination Mo species. The other strong reduction peak is around 760 ℃, belonging to the deep reduction ($Mo^{4+} + 2e \longrightarrow Mo^0$) of polymeric octahedral, tetrahedral and bulk crystalline MoO_3.[25] The temperature of reduction peaks in the H_2-TPR profiles directly reflect the strength of the interaction between the active metal components and the carrier. The peak locations at low temperature of the as-prepared catalysts increase as the following order: MoCo-D/δ < MoCo-N/δ < MoCo-A/δ < MoCo-S/δ , which indicate that the interaction between metal and carrier increasing as the above order. Furthermore, compared with other catalysts, a strong increase in the peak area in low temperature region and a considerable decrease in the high reduction temperature of tetrahedral Mo species are observed for MoCo-S/δ. These phenomena mean an increase in the proportion of the dispersed octahedral Mo species which are easy to be reduced as they are promoted by cobalt sulfate, consequently it will probably favor the formation of a mixed Co-Mo-S phase.

3.1.4 Raman characterization of the oxide MoCo catalysts

As shown in Fig.4, the Raman spectra of MoCo/δ-Al_2O_3 catalysts with different cobalt salts show main characteristic peaks of 250、331、564、839、945 and 980 cm^{-1}. The peaks of 839 cm^{-1} and 331 cm^{-1} are attributed to the bending vibration of Mo=O bond in the tetrahedron coordination MoO_4^{2-}. The peak of 945 cm^{-1},[26] which is considered to be the signals of the weak interaction between the metal and carrier, are relatively easy to be deoxidized and sulfided in the presulfurization process. Only the characteristic peak of the bending vibration of Mo=O bond, derived from the tetrahedron coordination MoO_4^{2-}, is found in the Raman spectra of Mo/δ-Al_2O_3. The characteristic peak of the vibration of Mo=O bond in $Mo_7O_{24}^{6-}$ appears after the introduction of Co into catalysts, indicating that Co has a great influence on the atom state of Mo over the catalyst surface and makes Mo better dispersion.

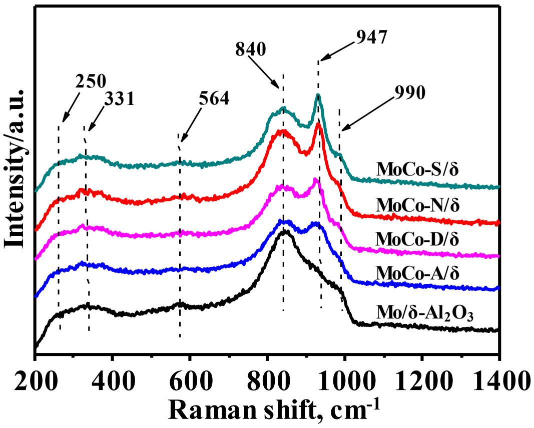

Fig. 4. Raman spectra of the MoCo/δ catalysts with different cobalt salts.

After the loading of Co, the intensity of peak of 945 cm^{-1} attributing to the vibration of Mo=O in $Mo_7O_{24}^{6-}$, increases as the following order: MoCo-A/δ < MoCo-N/δ < MoCo-D/δ < MoCo-S/δ, demonstrating that the Mo species of the MoCo catalyst based on cobalt sulfate are easier to be deoxidized and sulfided, which is in accordance with the results of H_2-TPR. Besides, the peak of 990 cm^{-1}, which is ascribed to the bulk MoO_3, are not found, meaning no aggregation of active metal. The unobvious peak of 564 cm^{-1}, which derives from the Al-O stretching vibration accounting for the interaction between the alumina carrier and the active metal, implys the weak metal-support interaction(MSI) over the δ-Al_2O_3 supported catalysts is beneficial for the reduction and sulfidation of active metal.

3.1.5 XPS characterization of the sulfide CoMo catalysts

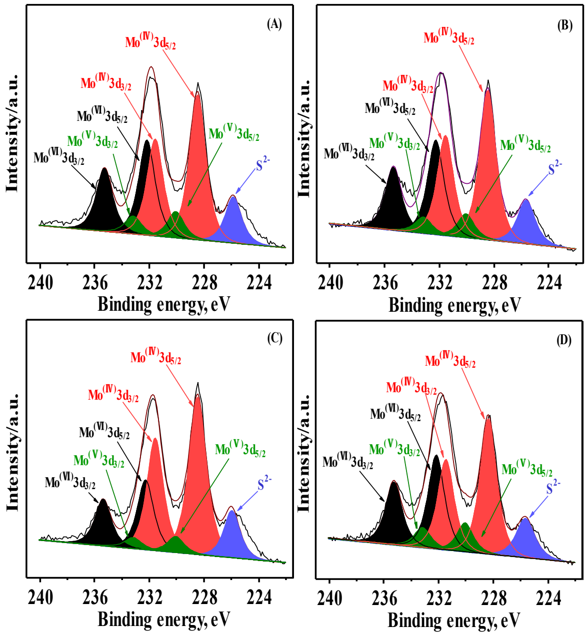

Fig. 5. Mo3d XPS spectra of the sulfided MoCo/δ catalysts with different cobalt salts.（A）MoCo-A/δ;（B）MoCo-N/δ;（C）MoCo-D/δ（D）MoCo-S/δ.

Table 1. XPS characterization results of the series of MoCo sulfided catalysts.

Catalysts	Mo^{4+}		Mo^{5+}		Mo^{6+}		S_{Mo} [b]
	ar. % [a] (228.9 eV)	ar.% (232.0 eV)	ar. % (230.5 eV)	ar. % (233.6 eV)	ar.% (232.5 eV)	ar.% (235.6 eV)	
MoCo-A/δ	36	24	5	3	20	13	60
MoCo-N/δ	38	25	3	2	19	13	63
MoCo-D/δ	39	26	2	2	18	12	65
MoCo-S/δ	41	27	2	2	17	11	68

Note: [a] ar. % means the area percent of XPS peak.

[b] $S_{Mo} = Mo_{sulfidation} = Mo^{4+}/(Mo^{4+}+Mo^{5+}+Mo^{6+})$.

XPS is a very useful characterization method to obtain the type and content of the active components on the surface of the sulfided HDS catalysts, and it is always used to analyze the sulfidation degree of Mo based catalysts. Fig.5 shows the Mo3d XPS spectra peak fitting results of the sulfided MoCo/δ catalysts with different cobalt salts. The XPS analysis results proceeded by the XPSPEAK 4.1 software are shown in Table 1. The standards for the fitting are as follow: the binding energies of $Mo3d_{5/2}$ and $Mo3d_{3/2}$ of Mo^{4+}(MoS_2) are 228.9±0.1 eV and 231.7±0.1 eV, respectively; while those for Mo^{5+} (MoS_xO_y) are 230.2±0.1 eV and 233.5±0.1 eV, and for Mo^{6+}(MoO_3) are 232.5±0.1 eV and 235.8±0.1 eV; [27] whereas the binding energy of S2s is 226.3±0.1 eV. [28] The sulfidation degree of the oxide Mo species, $Mo_{sulfidation}$, is calculated by $Mo_{sulfidation}= Mo^{4+}/(Mo^{4+}+Mo^{5+}+Mo^{6+})$ as listed in Table 1. The sulfidation degree of Mo species increases in the following order: MoCo-A/δ < MoCo-N/δ < MoCo-D/δ < MoCo-S/δ. MoCo-A/δ catalyst shows the lowest sulfidation degree (60%) of Mo species, while MoCo-S/δ catalyst exhibits the highest degree (68%). The XPS results demonstrate that Mo species over MoCo-S/δ catalyst are easy to be sulfided compared with other catalysts. Therefore, according to XPS analysis results, when the cobalt sulfate is used, Mo species can be dispersed and sulfided well, which is in consistent with the results of H_2-TPR.

3.2 Evaluation of HDS reactivity of FCC diesel

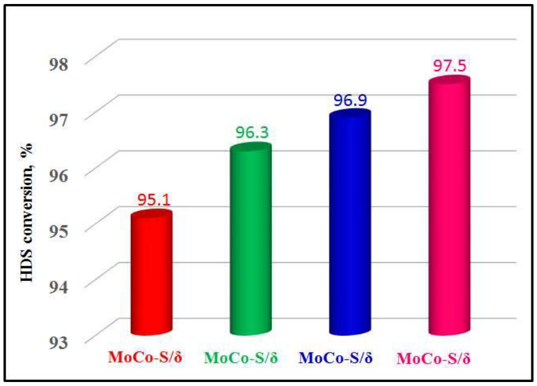

Fig. 6. HDS performances of the sulfided CoMo/δ catalysts with different cobalt salts.

Fig.6 shows the HDS reactivity results of the catalysts with different cobalt salts over δ-Al_2O_3 carriers. Different cobalt salts display significant influence on the hydrogenation activity of the catalysts. As for the catalysts with δ-Al_2O_3 as support, the hydrogenation activities of the catalysts increase in the following order: MoCo-A/δ < MoCo-N/δ < MoCo-D/δ < MoCo-S/δ. The catalyst with cobalt acetate as cobalt resource gives the lowest HDS activity (95.1%). However, the catalyst with cobalt sulfate as cobalt salts displays the highest desulfurization rate (97.5%).

According to the results of XRD and UV-vis spectra, the catalyst with cobalt sulfate as cobalt resource shows moderate content of β-$CoMoO_4$, and the active metal phases present smaller particle size and better dispersion when compared with other cobalt resources. The results of Raman confirm that the surface of the catalyst with cobalt sulfate as cobalt salts possesses more six coordination two-dimensional polymer $Mo_7O_{24}^{6-}$ which is easier to be deoxidized. Besides, H_2-TPR characterization shows that an increase in the proportion of the dispersed octahedral Mo species which are easy to be reduced when promoted by cobalt sulfate, indicating that it probably favors the formation of the mixed Co-Mo-S phases. XPS results also demonstrate the higher sulfurization degree of MoCo-S/δ catalyst. It has been reported that the catalysts with cobalt acetate and acetyl acetone cobalt as cobalt salts[29] showed better HDS activity, which was a little different from our results. On one hand, the possible reason is the different methods of the metal loading. On the other hand, the catalyst support used in this research is different with the supports reported. Through the analysis of characterization and evaluation of activity, it can be clearly seen that the HDS activity over MoCo-S/δ catalyst is the highest among this series catalysts, demonstrating that the introduction of cobalt sulfate can apparently promote the HDS performance of the MoCo/δ catalyst.

4. Conclusions

In this research, CoMo series catalysts were prepared by using low-cost δ-Al_2O_3 as support and different cobalt salts as promoter. The series of supported CoMo catalysts for HDS were characterized by UV-Vis, Raman, XRD, TPR, and XPS. The effects of different metal cobalt salts on HDS activity were explored systematically. This research provides a novel MoCo/δ-Al_2O_3 catalysts promoted by cobalt sulfate that can be used to the HDS reaction with high performance.

Different cobalt salts showed significant influences on the HDS activities of catalysts. As for the catalysts with δ-Al_2O_3 as support, the HDS activities of various catalysts increased in the following order: MoCo-A/δ< MoCo-N/δ< MoCo-D/δ< MoCo-S/δ. The catalyst with cobalt acetate as cobalt resource exhibited the lowest HDS efficiency (95.1%) and the catalyst with cobalt sulfate displayed the highest desulfurization degree (97.5%). These characterization results demonstrated that taking cobalt sulfate as promoter on the supported MoS_2 systems enabled to obtain a higher sulfidation degree (68%)

compared to the other cobalt promoters. These catalytic results could be ascribed to that the introduction of different cobalt salts decreased the MSI between metal and support, and led to the formation of easily reduced Mo species, which were the high active precursors to form more active sites that could enhance HDS activity of the catalysts. Moreover, Mo species could be dispersed and sulfided well when the different cobalt salts were used. Therefore, it can be concluded that the outstanding promoter effect endowed the MoCo-S/δ catalyst to be a promising catalyst for FCC diesel hydrotreating.

Acknowledgement

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Notes and References

1 I. Bezverkhyy, P. Afanasiev, M. Lacroix, J. Catal., 2005, **230**, 133-139.

2 V. C. Srivastava, RSC Adv., 2012, **2**, 759-783.

3 S. Eijsbouts, Appl. Catal. A, 1997, **158**, 53-92.

4 Y. Okamoto, K. Hioka, K. Arakawa, T. Fujikawa, T. Ebihara, T. Kubota, J. Catal., 2009, 268, 49-59.

5 D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal., 1998, **42**, 345-471.

6 H. TopsΦe, B.S. Clausen, R. Candia, C. Wivel, S. Mørup, J. Catal., 1981, **68**, 433-452.

7 J.A.R. van Veen, E. Gerkema, A.M. van Der Kraan, P.A.J.M. Hendriks, H. Beens, J. Catal., 1992, **133**, 112-123.

8 H. Farag, D.D. Whitehurst, K. Sakanishi, I. Mochida, Catal. Today, 1999, **50**, 9-17.

9 Y. Okamoto, S. Ishihara, M. Kawano, M. Satoh, T. Kubota, J. Catal., 2003, **217**, 12-22.

10 S.M.A. Bouwens, F.B.M. van Zon, M.P. van Dijk, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, D.C. Koningsberger, J. Catal., 1994, **146**, 375-393.

11 Y. Okamoto, A. Kato, Usman, N. Rinaldi, T. Fujikawa, H. Koshika, I. Hiromitsu, T. Kubota, J. Catal., 2009, 265, 216-228.

12 Y. Okamoto, J. Catal., 2008, **132**, 9-17.

13 H. Topsøe, B.S. Clausen, Appl. Catal., 1986, **25**, 273-293.

14 P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, H. Toulhoat, J. Catal., 2000, **190**, 128-143.

15 L.S. Byskov, B. Hammer, J.K. Norskov, B.S. Clausen, H. Topsoe, Catal. Lett., 1997, **47**, 177-182.

16 A. Travert, H. Nakamura, R.A. van Santen, S. Cristol, J.F. Paul, E. Payen, J. Am. Chem. Soc., 2002, **124**, 7084-7095.

17 H. Schweiger, P. Raybaud, H. Toulhoat, J. Catal., 2002, **212**, 33-38.

18 I. Bezverkhyy, P. Afanasiev, M. Lacroix, J. Catal., 2005, **230**, 133-139.

19 Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi, T. Kubota, Appl. Catal. A, 2002, **226**, 115-127.

20 J.L. Roustan, Y. Lijour, B.A. Morrow, Inorg. Chem., 1987, **26**, 2509-2516.

21 A.D. Gandubert, E. Krebs, C. Legens, D. Costa, G. Guillaume, P. Raybaud, Catal. Today, 2008, **130**, 149-159.

22 Y. Saih, M. Nagata, T. Funamoto, Y. Masuyama, K. Segawa, Appl. Catal. A, 2005, **295**, 11-22.

23 J. Ramiréz, P. Castillo, L. Cedefio, R. Cuevas, M. Castillo, J. Palacios, A.L. Agudo, Appl. Catal. A, 1995, **132**, 317-334.

24 J. Ojeda, N. Escalona, J.M. Palacios, M. Yates, J.L.G. Fierro, A.L. Agudo, F.J.G. Llambias, Appl. Catal. A, 2008, **350**, 6-15.

25 S. Damyanova, A. Spojakina, K. Jiratova, Appl. Catal. A, 1995, **125**, 257-269.

26 E. Payen, J. Grimblot, S. Kasztelan, J. Phys. Chem., 1987, **91**, 6642-6648.

27 J. Muijsers, T. Weber, R. Vanhardeveld, H.W. Zandbergen, J. Niemantsverdriet, J. Catal., 1995, **157**, 698-705.

28 T. Fujikawa, M. Kato, T. Ebihara, K. Hagiwara, J. Jpn. Petrol. Inst., 2005, **48**, 114-120.

29 D. Laurenti, B. Phung-Ngoc, C. Roukoss, E. Devers, K. Marchand, L.Massin, L. Lemaitre, C. Legens, Q. Anne-Agathe, M. Vrinat, J. Catal., 2013, **297**, 165-175.

GRAPHICAL ABSTRACT

In this paper, the supported MoCo/δ-Al_2O_3 catalysts promoted by different organic and inorganic cobalt salts were synthesized successfully by an incipient-wetness impregnation method. The active metal-support interaction(MSI) were adjusted by incorporating cobalt nitrate, cobalt sulfate, cobalt acetate, cobalt diacetylmethane into the framework of MoO_3/Al_2O_3, which could provide suitable MSI for ultra deep HDS to meet the high quality specifications of diesel. The HDS activities of various catalysts increased in the following order: MoCo-A/δ< MoCo-N/δ< MoCo-D/δ< MoCo-S/δ. As a result, the outstanding promoter effect endowed MoCo-S/δ to be a promising catalyst for FCC diesel hydroupgrading.