Ni and Co promoted MoW alumina supported HDS catalysts prepared from mixed $SiMo_3W_9$ heteropolyacids

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Abstract: Unpromoted and Ni/Co-promoted MoW HDS catalysts supported on alumina were prepared using mixed $H_4SiMo_3W_9O_{40}$ heteropolyacid and mixture of $SiMo_{12}$ and SiW_{12} HPAs. All catalysts were characterized by N_2 physisorption, HRTEM, XPS and evaluated in hydrodesulfurization of dibenzothiophene (DBT) and naphthalene hydrogenation (HYD). It was found that both Ni/Co-MoW catalysts prepared from mixed HPA showed better performance in HDS of DBT and HYD of naphthalene than their counterparts prepared from two separate monometallic HPAs. Ni-promoted catalysts exhibited higher catalytic activity compared to Co-promoted ones.

Keywords: Hydrotreating, Heteropolyanion, NiMoWS.

1. Introduction

Developing highly active hydrodesulfurization (HDS) catalysts has been one of the most challenging and important subjects because of strengthening of environmental requirements for the sulfur content in fuels. Traditionally, bimetallic sulfide catalysts based on Mo or W, promoted by Ni or Co and supported on Al_2O_3 are used in the HDS processes. One of the approaches to improve catalytic activity can the development of mixed MoW based catalysts. In this investigation, we report the synthesis and characterization of MoW catalysts promoted by Ni or Co prepared by using mixed $H_4SiMo_3W_9O_{40}$ heteropolyacid (HPA) of Keggin structure.

2. Experimental

Unpromoted and Ni/Co-promoted Mo(W) catalysts with the same surface density of metals - d(Mo+W) expressed by at.nm^{-2} - were synthesized by incipient wetness method impregnation of the supports with aqueous solutions containing the required amounts of SiW_9Mo_3HPA, Ni or Co citrate with molar ratio Ni(Co)/(W+Mo) = 0.5. Moreover, the catalysts based on monometallic SiW_{12}HPA and mixture of $SiMo_{12}$ and SiW_{12}HPAs were prepared as references. The chemical composition of the synthesized catalysts is shown in Table 1.

Table 1. Chemical composition of prepared catalysts.

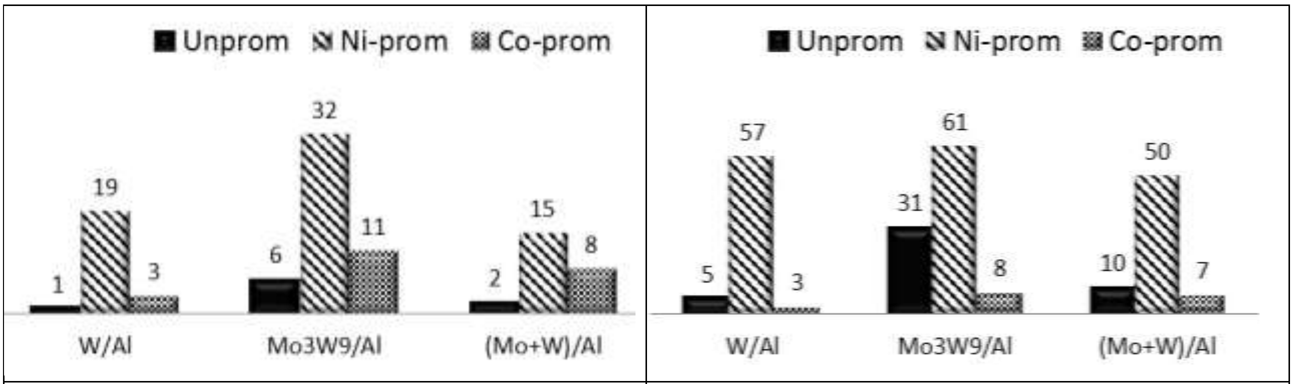
Catalyst	MoO_3, wt.%	WO_3, wt.%	NiO/CoO, wt.%	d(Mo+W), at.nm^{-2}
(Ni/Co)-W/Al		26.2	4.2	4.0 (4.2) *
(Ni/Co)-Mo_3W_9/Al	4.2	20.1	4.3	4.0 (4.2)
(Ni/Co)-(Mo+W)/Al	4.2	20.1	4.3	4.0 (4.2)

*density of metals d(Mo+W) calculated for Ni(Co)-promoted catalysts.

The hydrotreatment activities were measured on a model feed (1000 ppm of sulfur, 3 wt. %. of naphthalene and toluene as a solvent) in a bench-scale flow reactor under pressure of hydrogen. Before testing, the catalysts were activated by sulphidation. A mixture of DMDS (2 wt. % of S) and decane at 3.5 MPa was used in a stepwise procedure conducted over 10 h at 240 ºC and 8 h at 340 ºC. The conditions of the tests were the following: temperature 280 ºC; pressure 3.0 MPa; feed space velocity 5 h^{-1} (unpromoted samples) and 40 (promoted catalysts); a H_2 feedstock ratio 500 NL/L. The liquid product compositions of the samples collected every 0.5 h were determined using a GCMS-QP2010 Ultra. The HDS reaction was allowed to proceed for 10 h to obtain the steady-state activity of the catalysts. To evaluate the catalytic performances, rate constants of the DBT HDS and naphthalene HYD reactions were determined

3. Results and discussion

Figure 2 shows the hydrotreating results for the mixture of DBT and naphthalene over the prepared samples.



a - dibenzothiophene HDS

b - naphthalene hydrogenation

Figure 1. Dependence of the rate constants of the HDS DBT (a) and HYD naphthalene (b) reactions over Ni(Co)Mo(W)/Al catalysts on their chemical composition.

It was found, that the introduction of Mo from mixed precursor led to increasing HDS and HYD activities compared to that of SiW_{12}HPA based catalysts. As a result, all MoW containing reference samples prepared from two separate HPAs had lower catalytic activity than their counterpart based on mixed SiW_9Mo_3HPA. These results witness in favor of the creation of more active mixed $Mo_xW_{1-x}S_2$ active sites.

The formation of mixed $Mo_xW_{1-x}S_2$ slabs when mixed HPA was used for preparation of unpromoted catalyst was evidenced by EXAFS and HAADF analysis[1]. Taking into account the above results, it can be assumed the creation of mixed Ni(Co)MoWS mixed active sites in case of promoted series. Then the low catalytic activity of Co-Mo_3W_9/Al compared to Ni-Mo_3W_9/Al is in good agreement with the reported DFT calculations[2] where P. Raybaud and co-workers predicted a synergetic effect for Ni promoted $Mo_{1-x}W_xS_2$ active phases relative NiMoS and NiWS ones and no synergetic effect for $CoMo_{1-x}W_xS_2$ phases with respect to CoMoS and CoWS ones.

4. Conclusions

It was found that the use of mixed $SiMo_3W_9$HPA as starting precursor yield high-efficient HDT catalysts. Mixed HPA based catalysts were more active in DBT HDS and naphthalene HYD reactions in contrast to their Mo+W references with the same surface density of the metals prepared from two separate monometallic HPAs.

References

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