Comparative study of CoMo/MWCNT and CoMo/Al_2O_3 Hydrotreating Catalysts Prepared with Citric Acid

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Abstract: In this work the effects of MWCNT and γ-Al_2O_3 supports on the properties and hydrodesulfurization (HDS) activity of corresponding CoMo catalysts prepared by impregnation with aqueous solution of metal precursors and citric acid has been studied. The proportion of active metals in the form of CoMoS phase is higher for CoMo/MWCNT catalyst. The latter provides beneficial effect on HDS and hydrogenation activity.

Keywords: hydrotreating, Co-Mo-S catalyst, multi-walled carbon nanotubes.

1. Introduction

Hydrotreating processes are largely carried out over sulfided Co(Ni)Mo catalysts supported on alumina, which has good thermal, mechanical and textural properties and provides high dispersion of the active metal components. However, the main drawback of alumina is strong interaction with the active components, which hinders the complete sulfidation of supported metals and decreases the number of active sites. There are number of approaches for preparation of hydrotreating catalysts with enhanced activity. Among them, the addition of chelating agents, especially, citric acid as a relatively inexpensive chelating agent, has been widely used in the hydrotreating catalysts preparation. Unlike alumina, carbon materials hydrophobic surface limits the metal support interaction, which facilitates the sulfidation process. Multi-walled carbon-nanotubes (MWCNT) have drawn a lot of attention since their discovery due to their unique properties. In this work the effects of MWCNT and γ-Al_2O_3 supports on the properties and hydrodesulfurization (HDS) activity of corresponding CoMo catalysts prepared with citric acid is studied.

2. Experimental

MWCNT were synthesized by CVD of ethylene decomposition over the bimetallic Fe-Co catalysts at 680°C. The functionalized MWCNT containing surface carboxylic groups (0.76 groups per 1 nm^2) were obtained via boiling in concentrated nitric acid. For CoMo/MWCNT catalyst preparation the functionalized MWCNT were used. The Al_2O_3 support was prepared by extrusion of boehmite paste using plunger extruder with subsequent drying of obtained trilobe extrudates at 120°C and calcination at 550°C. CoMo/MWCNT and CoMo/Al_2O_3 catalysts were prepared by impregnation with aqueous solution prepared from cobalt hydroxide, ammonium heptamolybdate and citric acid. Impregnated catalysts were dried at 120°C. The catalysts contained 12.0 ± 0.2 wt% of Mo and 3.2 ± 0.1 wt% of Co. The sulfidation of the catalysts was carried out in H_2S flow for 4 h at 200°C and 400°C at atmospheric pressure. The catalysts in sulfide form were studied by N_2 physisorption, XPS and HRTEM. The catalysts were tested in simultaneous dibenzothiophene (DBT) HDS and naphthalene hydrogenation in fixed-bed reactor under the following conditions: $t = 280°C$, $P = 3.5$ MPa, LHSV 20 h^{-1}, H_2/feed = 500 nm^3/m^3.

3. Results and discussion

Figure 1 shows HRTEM data for sulfide CoMo/MWCNT and CoMo/Al_2O_3 samples. For both catalysts the unsulfided species of active component are not observed. Active phase is uniformly distributed on Al_2O_3 surface in CoMo/Al_2O_3 catalyst. For CoMo/MWCNT the presence of active phase both inside and outside the CNT channels is observed. The average stacking number and slab length were calculated for each catalyst using not less than 500 slabs. It is defined that the average stacking number for CoMo/MWCNT and CoMo/Al_2O_3 samples is close and equal to 1.035±0.015. The average slab length is 2.88 nm for CoMo/Al_2O_3 and 3.75 nm for CoMo/MWCNT.

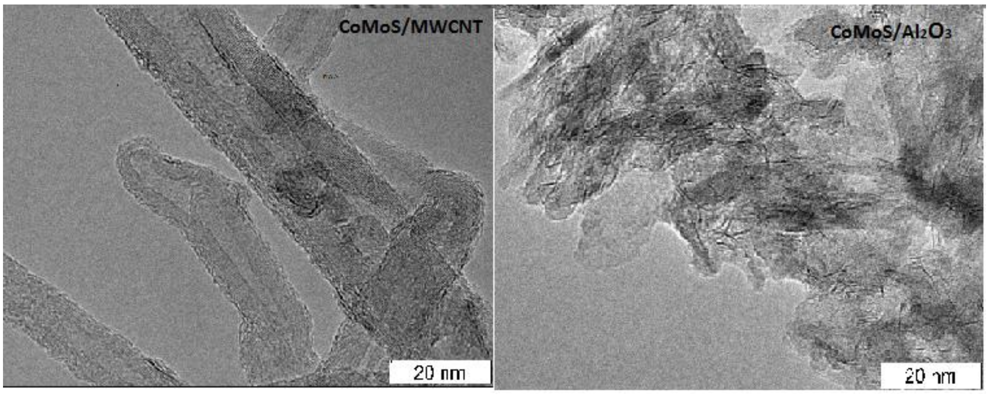

Fig. 1. TEM micrographs of sulfide CoMo/MWCNT and CoMo/Al_2O_3 samples

The formation of active CoMoS phase on the surface of supports was confirmed by XPS. For both catalysts Mo3d spectra contain an intensive peak with binding energy of 229±0.1 eV and Co2p spectra contain an intensive peak with binding energy of 779.0±0.1 eV. According to Mo3d spectra decomposition the amount of Mo^{4+}, which is related to molybdenum in sulfur surrounding in sulfide catalysts, is higher for CoMo/MWCNT sample: 77% versus 63% for CoMo/Al_2O_3. The decomposition of Co2p spectra shows that the amount of CoMoS phase is 73% for CoMo/MWCNT and 63% for CoMo/Al_2O_3.

Table 1. DBT and naphthalene conversion over CoMo/MWCNT and CoMo/Al_2O_3 catalysts

Sample	**Conversion, %**	
	DBT	**Naphthalene**
CoMo/MWCNT	91.6	12.4
CoMo/Al_2O_3	80.8	8.8

The results of catalysts testing in hydrotreating of model feed (Table 1) show that CoMo/MWCNT has higher activity in HDS of DBT and hydrogenation of naphthalene.

4. Conclusions

Comparative study of CoMo/MWCNT and CoMo/Al_2O_3 hydrotreating catalysts prepared by impregnation with aqueous solution of metal precursors and citric acid has been performed. The proportion of active metals in the form of CoMoS phase is higher for CoMo/MWCNT catalyst. The latter provides beneficial effect on HDS and hydrogenation activity.

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