

THE THIOPHENE CONVERSION ON CARBON-SUPPORTED MOLYBDENUM CATALYSTS

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Introduction

In recent years carbon supported Mo-containing hydrotreating catalysts are intensively studied. The improved thiophene hydrodesulphurization (HDS) activity of the catalysts using the carbon support instead of alumina one has been shown [1]. Different types of carbons and a number of alternative methods have been used in preparation of molybdenum catalysts [2,3]. There are disagreements related to effect of the physical and chemical surface properties on the HDS activity of the carbon-supported catalysts.

In this laboratory effect of support and heteropoly compounds as precursors of active phase on the HDS activity of the Mo-containing catalysts is studied. This paper presents the thiophene conversion over carbon-supported catalysts using ammonium heptamolybdate (AHM) and 12-molybdophosphoric acid (HPMo) as molybdenum precursors.

Experimental

A commercially available activated carbon, A, (France, $S_{\text{BET}}=1230 \text{ m}^2\text{g}^{-1}$, $V_o=1.1 \text{ cm}^3 \text{ g}^{-1}$) and one originating from apricot stones, B, ($S_{\text{BET}}=525 \text{ m}^2\text{g}^{-1}$, $V_o=0.73 \text{ cm}^3\text{g}^{-1}$) were used as supports. There is no phosphorus in these carbons. Equilibrium pH of their slurries (1 g in 25 ml) was about neutral. Catalysts with Mo loading of 12 wt. % were prepared by the incipient wetness technique using aqueous solutions of AHM (pH 6) (samples MoA and MoB) and HPMo (pH 1.6) (samples PMoA and PMoB). The impregnated samples

were dried in air at 120°C during 6 h. The thiophene conversion was measured in a flow system at 350°C, atmospheric pressure and space velocity of 2 h⁻¹. Two types of pretreatments were applied to the samples: i) after heating in an Ar stream up to 350°C the catalysts were presulphided *in situ* by H₂S and purged with Ar; ii) the samples prereduced in H₂ at 350°C were sulphided by H₂S evolved during the thiophene HDS.

Results and Discussion

The thiophene conversion in hydrocarbons for all catalysts as a function of reaction time shows no notable difference in the steady state activity after 2 h on stream (Figs. 1 and 2). Phosphorus introduced with HPMo in the PMoA and PMoB catalysts during their preparation does not decrease the thiophene conversion in contrast to

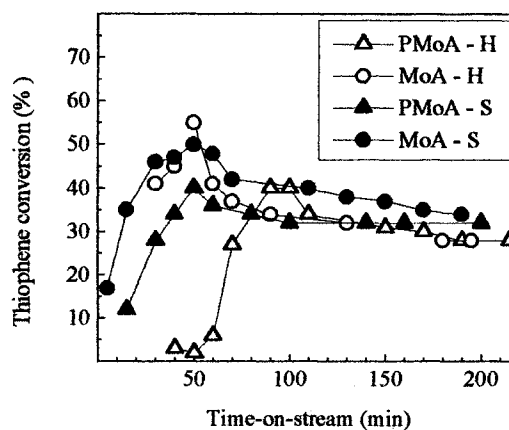


Figure 1. Thiophene conversion vs time-on stream over A-carbon-supported Mo catalysts after prereduction (-H) and presulphidation (-S).

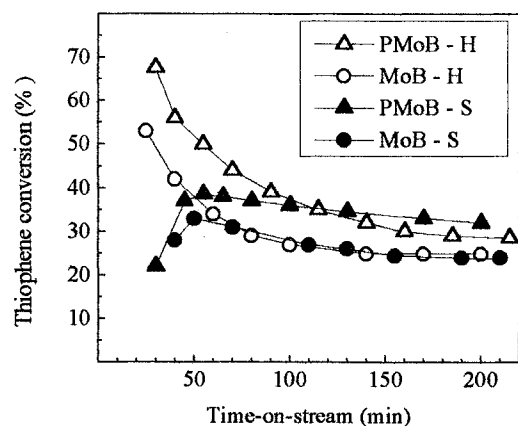


Figure 2. Thiophene conversion vs time-on-stream over B-carbon-supported Mo catalysts after prerreduction (-H) and presulphidation (-S).

results observed by Vissers et al. [4]. The difference in the carbons properties or the lower temperature could explain this result. The effect of the activated carbon, precursor of molybdenum and pretreatment of the catalysts on the HDS activity can be seen only in the initial stages of sulphidation of catalysts when the catalytic phase is produced. Butane and all butenes are detected in products of the thiophene conversion over the prerreduced MoA, PMoB and MoB samples. In contrast to these results only butane is revealed over PMoA sample at the first hour on stream. The flexibility of the carbon surface does possible it to be changed during impregnation of precursors. Most probably in this sample the strong oxidative ability of the HPMo leads to the formation on the carbon surface of the acid sites related to the thiophene hydrogenolysis in butane. The acidic activity of these sites decreases with a simultaneous sulphidation of Mo species by the H_2S evolved. After 1 h butenes appear in the products of the thiophene conversion as a result of the new sites formation.

All presulphided samples detect an increase of initially low activity as a result of the H_2S desorption from active sites [6]. It can be seen that the thiophene conversion over the presulphided samples easier reaches

the steady state activity in comparison to that of the prerreduced samples. A lower dispersion of Mo species after sulphidation could explain this result.

Complex surface chemistry of the activated carbons and catalysts and mutual transformation of the surface groups have been shown using FTIR spectra (to be submitted). In agreement with [2] the results obtained mean that at relatively high molybdenum content in catalyst Mo species do not strongly interact with the carbon surface. Mobility of the Mo species decreases the dispersion and activity of the samples after or during sulphidation.

Conclusion

The carbon peculiarities and interaction with precursor of catalyst as well as its activation affect the initial thiophene conversion. No meanful difference in the steady state activity of the studied catalysts is observed.

Acknowledgement

This work was supported by the National Foundation for Scientific Research - Bulgaria (Project X-462).

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