Nickel-rich Bimetallic Phosphide Hydrotreating Catalysts

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Introduction

Oxide-supported transition metal phosphides, nickel phosphide (Ni_2P) in particular, have recently been shown to have high hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities [1]. In previous work from our laboratory, silica-supported Ni_2P was found to be over three times more active than a sulfided Ni-Mo/SiO_2 catalyst (Ni/Mo = 0.5) for the HDS of thiophene [2]. In this presentation, the effects of incorporating a second metal into nickel phosphide catalysts ($Me_xNi_{2-x}P$; Me = Co, Fe, Mo; $0 < x \leq 1$) will be reported.

Materials and Methods

Silica-supported Ni_2P, Co_2P, Fe_2P and $Me_xNi_{2-x}P$ (Me = Co, Fe, Mo; $0 < x \leq 1$) catalysts were prepared by temperature programmed reduction (TPR) of oxidic precursors in flowing hydrogen, following procedures adapted from one described previously [3]. The catalysts were characterized with a range of physicochemical techniques and thiophene HDS activity measurements (643 K, 3.2 mol% thiophene/H_2) were carried out using an atmospheric pressure flow reactor which has been described in detail elsewhere [2,3]. For comparison purposes, thiophene HDS activity measurements were also carried out for sulfided Ni-Mo/SiO_2 (Ni/Mo = 0.5) catalysts.

Results and Discussion

Thiophene HDS activities were measured for the silica-supported Me_2P and $Me_xNi_{2-x}P$ catalysts and these are plotted in Figure 1 as a function of the Ni content. While $Mo_xNi_{2-x}P$ catalysts have lower HDS activities than either MoP or Ni_2P, $Co_xNi_{2-x}P$ and $Fe_xNi_{2-x}P$ catalysts show a trend of increasing HDS activity with increasing Ni content with some of the Ni-rich bimetallic phosphide compositions having higher HDS activities than Ni_2P. Silica-supported $Me_xNi_{2-x}P$ materials with Me = Co or Ni and x ~ 0.08 have HDS activities over 30% higher than does a Ni_2P/SiO_2 catalyst prepared similarly. Listed in Table 1 are the bulk and surface compositions of selected silica-supported monometallic and bimetallic phosphide catalysts, as well as the surface compositions of some of these catalysts after HDS testing. The surfaces of the monometallic phosphide catalysts are enriched in metal relative to the bulk compositions, while the opposite is true for the $Co_xNi_{2-x}P$ and $Fe_xNi_{2-x}P$ catalysts with x ~ 0.08. The addition of a small amount of a second metal (Co, Ni) leads to surface enrichment in P, and the post-HDS surface compositions indicate that these catalysts are quite resistant to S incorporation under reaction conditions.

Significance

Nickel-rich bimetallic phosphide catalysts containing small amounts of Co or Ni exhibit high thiophene HDS activity and strong resistance to S incorporation under reaction conditions. These materials show promise as the active phase in non-sulfide hydrotreating catalysts.

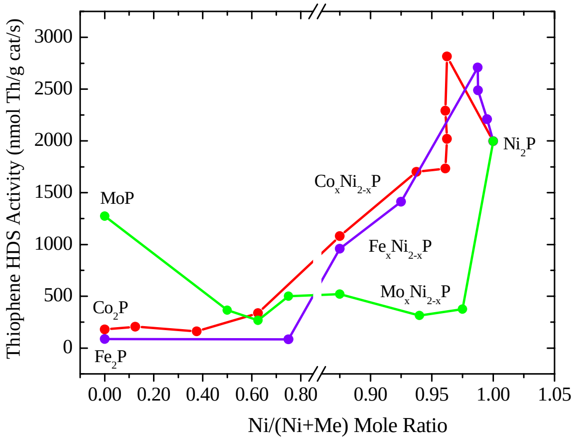

Figure 1. Thiophene HDS activity for $Me_xNi_{2-x}P$ as a function of the Ni content.

Table 1. Bulk and Surface Compositions of Silica-supported Metal Phosphide Catalysts

Nominal Composition	Bulk Composition	Surface Composition	Surface Composition (post HDS)
Co_2P	$Co_{1.88}P_{1.00}$	$Co_{3.46}P_{1.00}$	-----
$Co_{1.50}Ni_{0.50}P$	$Co_{1.33}Ni_{0.46}P_{1.00}$	$Co_{1.02}Ni_{0.27}P_{1.00}$	-----
$Co_{0.25}Ni_{0.1.75}P$	$Co_{0.23}Ni_{1.60}P_{1.00}$	$Co_{0.28}Ni_{1.51}P_{1.00}$	-----
$Co_{0.08}Ni_{0.1.92}P$	$Co_{0.060}Ni_{1.51}P_{1.00}$	$Co_{0.085}Ni_{1.01}P_{1.00}$	$Co_{0.13}Ni_{1.59}P_{1.00}S_{0.064}$
Ni_2P	$Ni_{1.64}P_{1.00}$	$Ni_{2.234}P_{1.00}$	-----
Fe_2P	$Fe_{1.77}P_{1.00}$	$Fe_{4.00}P_{1.00}$	$Fe_{3.37}P_{1.00}S_{0.30}$
$Fe_{0.50}Ni_{1.50}P$	$Fe_{0.46}Ni_{1.36}P_{1.00}$	$Fe_{0.45}Ni_{1.64}P_{1.00}$	$Fe_{0.58}Ni_{1.89}P_{1.00}S_{0.18}$
$Fe_{0.25}Ni_{0.1.75}P$	$Fe_{0.23}Ni_{1.64}P_{1.00}$	$Fe_{0.47}Ni_{1.52}P_{1.00}$	$Fe_{0.36}Ni_{1.16}P_{1.00}S_{0.057}$
$Fe_{0.08}Ni_{1.92}P$	$Fe_{0.072}Ni_{1.76}P_{1.00}$	$Fe_{0.32}Ni_{1.14}P_{1.00}$	$Fe_{0.36}Ni_{1.16}P_{1.00}S_{0.091}$
Ni_2P	$Ni_{1.64}P_{1.00}$	$Ni_{2.23}P_{1.00}$	-----

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