Synthesis and Properties of Metal Phosphide Hydrotreating Catalysts Containing Noble Metals

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Introduction

The high impurity levels in heavy and unconventional crude oils present major challenges to the petroleum industry at a time that environmental regulations are dramatically lowering allowable sulfur levels in transportation fuels [1]. Supported metal phosphides, particularly Ni_2P/SiO_2, have exhibited high hydrodesulfurization (HDS) activities [2,3]. More recently, investigation of Ni-rich bimetallic phosphides has indicated that incorporation of a second metal can improve the HDS properties of nickel phosphide [4]. An important property of metal phosphide catalysts is a strong resistance to S incorporation under HDS conditions. Current research focuses on the synthesis and HDS properties of noble metal phosphides and of bimetallic phosphides containing noble metals. These materials are being targeted as potential HDS catalysts because oxide-supported noble metals have been shown to be highly active for deep HDS, but are prone to sulfur poisoning [1].

Materials and Methods

Noble metal phosphides (Ru_xP_y, Rh_xP_y, Pd_xP_y) and bimetallic phosphides (e.g. $Rh_xNi_{2-x}P$) supported on silica have been prepared using temperature-programmed reduction (TPR) of metal phosphate precursors following procedures adapted from those described previously [3,4]. The catalysts were characterized with a range of physicochemical techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and pulsed chemisorption. Thiophene HDS activity measurements were carried out using an atmospheric pressure flow reactor and preliminary dibenzothiophene HDS measurements have been conducted in a newly constructed high pressure reactor system. For comparison purposes, thiophene HDS activity measurements were also carried out for a sulfided Ni-Mo/SiO_2 catalyst (Ni/Mo = 0.5, 7.9 wt% NiO, 30.4 wt% MoO_3).

Results and Discussion

A number of metal phosphides of Ru, Rh and Pd have been prepared on high surface area silica by optimization of the precursor composition (P/Me molar ratio) and TPR parameters. For example, silica-supported Rh_2P was prepared from a calcined precursor having P/Rh = 0.75 and a maximum TPR temperature of 923 K. An XRD pattern of a 20 wt% Rh_2P/SiO_2 catalyst is compared to a reference pattern from the powder diffraction file (card #002-1299) in Figure 1; the excellent agreement of the two patterns indicates the phase purity of the supported Rh_2P. Based on XPS measurements, the surface composition of the supported Rh phosphide particles was determined to be $Rh_{0.94}P_{1.00}$. The 20 wt% Rh_2P/SiO_2 catalyst was observed to be highly active for thiophene HDS, with an activity 3.4 times higher than that of 20 wt% Ni_2P/SiO_2 and ten times more active than the sulfided Ni-Mo/SiO_2 catalyst. The comparisons were based on the HDS activities after 48 h on-stream. An XRD pattern of a post-HDS 20 wt% Rh_2P/SiO_2 catalyst, shown in Figure 1, indicates no change in the crystalline

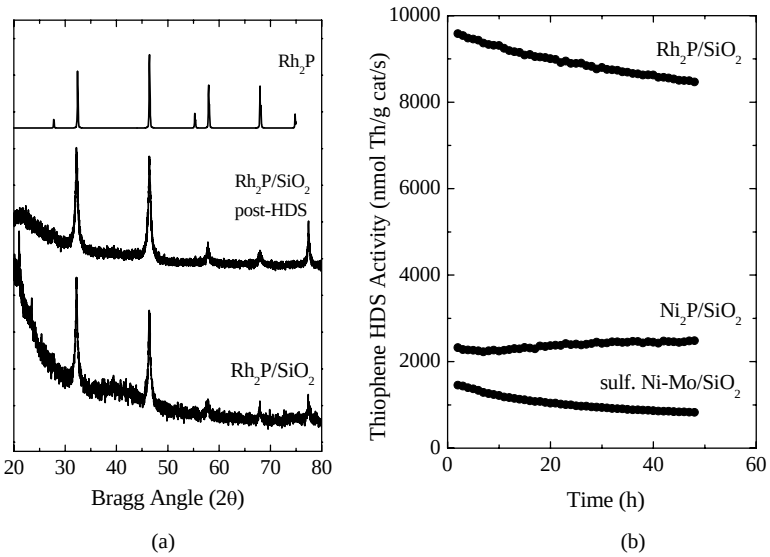

Figure 1. (a) XRD patterns for freshly prepared and tested Rh_2P/SiO_2 catalysts and (b) HDS activity data for silica-supported Rh_2P, Ni_2P and sulfided Ni-Mo catalysts.

structure of the supported Rh phosphide particles occurred during HDS testing over a 48 h period. XPS analysis of the post-HDS Rh_2P/SiO_2 catalyst revealed the surface composition of the catalyst to be $Rh_{0.96}P_{1.00}S_{\leq 0.01}$. The surface composition of the post-HDS catalyst is unchanged from that of the fresh catalyst with the S content below the detection limit of the spectrometer.

Significance

Preliminary studies of noble metal phosphides and bimetallic phosphides containing noble metals suggest that these are promising catalytic materials for use in HDS processing

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