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EXAFS Investigation of Transition Metal Phosphide Catalysts

S. T. Oyama and Y. Lee (Virginia Tech)

Beamline(s): X18B

Introduction: Transition metal phosphides have traditionally found uses as semiconductors, luminescent devices, and electronic components. Recently our group has discovered that they are excellent catalysts for the removal of sulfur and nitrogen from petroleum feedstocks, with activities higher than commercial catalysts [1,2]. This has been an important discovery, as advanced refining catalysts are urgently needed to deal with increasingly more difficult crudes and stricter environmental standards.

Methods and Materials: Nickel phosphide catalysts supported on USY zeolite were prepared by impregnation of the support with nickel nitrate (Aesar, 99%) and ammonium phosphate (Aldrich, 99%) followed by calcination at 773 K and temperature programmed reduction to 900 K. Two loadings were prepared with Ni contents of 1.2 and 1.7 mmol/g. Samples for XAFS measurements were loaded in glass cells with Kapton atmosphere and sealed without exposure to the atmosphere. Reactivity measurements in hydro processing were made in an up flow, three phase reactor at 3.1 MPa (450 psig) and 643 K (370°C) with a H_2 flow rate of 100 μmol s^{-1} (150 cm^3 min^{-1}). The feed liquid consisted of 500 wppm S as dimethyldibenzothiophene (Aldrich, 99 %), 2000 wppm N as quinoline (Aldrich, 99 %), 20 % tetralin (Aldrich 99 %), and balance hexadecane (Fisher, 99 %), and was delivered at 5 cm^3 h^{-1}.

Results: The Ni_2P/USY samples were highly active in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), with activity in HDS higher than a commercial Ni-Mo-S/Al_2O_3 catalyst.

Catalyst	HDS	HDN
Ni-Mo-S/Al_2O_3	53	94
Ni_2P/SiO_2	43	100
Ni_2P/USY (1.156)	80	85

X-ray diffraction showed Ni_2P lines only for the high loading (1.7 mmol/g) sample. EXAFS analysis, however, showed the presence of Ni_2P in both samples. The active phase in the low loading sample (1.2 mmol/g) was clearly highly dispersed.

Conclusions: A highly active nickel phosphide catalyst supported on USY zeolite was prepared. EXAFS was instrumental in identifying the phase composition.

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References:

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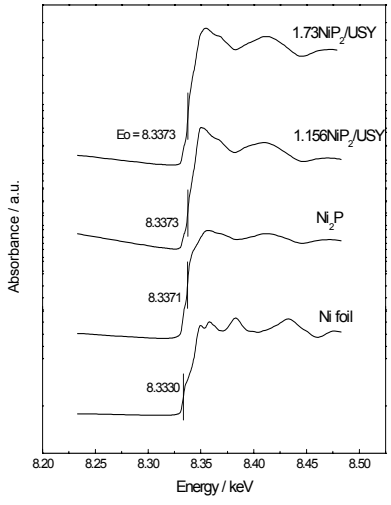

Figure 1. Near-Edge X-Ray Absorption

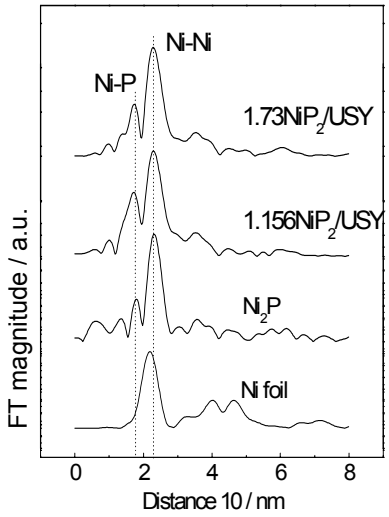

Figure 2. EXAFS