

New Approaches to the Synthesis of Highly HDS Active Silica-Supported Nickel Phosphide Catalysts

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Introduction

The declining quality of petroleum feedstock has made the removal of sulfur from crude oils one of the most challenging tasks for the refining industry in order to respect environmental regulations. More efficient hydrodesulfurization (HDS) catalysts are therefore needed. This can be achieved either using new methods of preparations for the well-known Co(Ni)Mo/Al₂O₃ catalysts or through the synthesis of new active phases. In recent years, transition metal phosphides have been found to be excellent HDS catalysts, particularly Ni₂P/SiO₂ [1]. Extensive studies have then been performed on this catalytic system and a phosphosulfide active phase was found to be responsible for such a high activity [2].

However, nickel phosphides are commonly obtained through the reduction at high temperature (650°C) of nickel phosphates. This high temperature treatment made their application as possible industrial HDS catalysts quite limited. In order to make these catalysts more attractive, alternative approaches using low temperature procedures have to be found. This can be done using precursors than can readily form nickel phosphides at low temperatures. In previous studies, Robinson et al. [3] have found that nickel thiophosphate (NiPS₃) obtained by solid state techniques can be decomposed into nickel phosphides during the course of an HDS reaction. In the present study, nickel thiophosphates have therefore been synthesized but using soft chemistry routes before being reduced at low temperature (250°C) to obtain silica-supported nickel phosphide catalysts. This approach was compared to a “more classical” nickel phosphate-nickel phosphide route. Results showed that active HDS Ni_xP_y/SiO₂ catalysts can be obtained using this approach. The influence of the P/Ni molar ratio of the final catalysts was particularly studied

Materials and Methods

The NiPS₃ precursor was synthesized at room temperature through the reaction of NiCl₂ with Li₂PS₃ according to the method developed by Prouzet and co-workers [4]. The as-formed nickel thiophosphate was then diluted into ethanol, impregnated onto silica and reduced at low temperature (250°C) to obtain Ni₂P/SiO₂. For comparison purposes, nickel phosphides were also prepared through the reduction of nickel phosphates. In this case, in a first step, NiNH₄PO₄·H₂O was prepared by reaction between NH₄H₂PO₄ and Ni(NO₃)₂·6H₂O. After impregnation onto silica, NiNH₄PO₄·H₂O was reduced at 550°C for 12 h to obtain silica-supported nickel phosphides. The thiophosphate and nickel phosphide compounds

(unsupported and silica-supported) were characterized by TEM, (in situ) XRD, Laser Raman spectroscopy (LRS), magnetic susceptibility, ³¹P NMR, and EXAFS.

Results and Discussion

In a first step, unsupported well-crystallized NiPS₃ was synthesized using solid state techniques and characterized using ³¹P NMR, XRD, LRS, and EXAFS. This well-crystallized NiPS₃ was then used in a second step as a reference compound. The nickel thiophosphate obtained using soft chemistry approach showed a poorly crystallized phase which can be however ascribed to NiPS₃ through comparison to the well-crystallized reference. After deposition onto SiO₂, Raman spectroscopy studies evidenced that the NiPS₃ phase was preserved. However, during the HDS of thiophene, NiPS₃ is transformed into a more active Ni₂P phase. Similarly, reductive pre-treatment before HDS showed that depending on the temperature of reduction, Ni₂P/SiO₂ or Ni₅P₄/SiO₂ catalysts could be obtained. Complementary results obtained through the reduction of nickel phosphates suggest that Ni₅P₄/SiO₂ is intrinsically more active in HDS than Ni₂P/SiO₂ and NiMo/Al₂O₃. For instance, Ni₅P₄/SiO₂ presents a thiophene HDS activity 50 % higher (per gram of active phase) than the one obtained on a NiMo/Al₂O₃ catalyst. Finally, in situ XRD studies coupled with EXAFS and magnetic susceptibility results bring new information about the reduction process of nickel phosphate into nickel phosphide. Indeed, the initially well-crystallized nickel phosphide is transformed progressively into an amorphous phosphate phase between 300 and 500°C before phosphide formation.

Significance

Alternative approaches have been developed to synthesize silica-supported nickel phosphides using low-temperature treatment of nickel thiophosphate precursors. This led to the formation of Ni₂P/SiO₂ catalysts at reduction temperatures as low as 250°C. The as-formed catalysts are active in the HDS of thiophene. Moreover, analysis of the different Ni_xP_y phases formed showed that Ni₅P₄/SiO₂ is a very highly active HDS catalyst.

References

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