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Ni_2P/Al_2O_3 hydrodesulfurization catalysts prepared by separating the nickel compound and hypophosphite

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ABSTRACT

Bulk Ni_2P and Al_2O_3-supported Ni_2P were prepared at low phosphidation temperature (300 or 330 °C) from nickel nitrate, oxide, sulfate, chloride, and acetate as nickel source and ammonium and sodium hypophosphite as well as hypophosphoric acid as phosphorus source. The hypophosphite source was positioned up-flow of the nickel source in an oven and flowing N2 gas transported the phosphine formed in the decomposition of hypophosphite to the nickel compound. X-ray diffraction, N2 adsorption-desorption, thermogravimetry and differential scanning calorimetry, temperature-programmed reduction in H_2, and transmission electron microscopy, field emission scanning electron microscopy, CO chemisorption, and solid-state ^{31}P nuclear magnetic resonance were used to study the bulk and supported Ni_2P. Whereas unsupported nickel nitrate, sulfate, chloride, and oxide led to impure Ni_2P, nickel acetate gave pure Ni_2P. Ni_2P/Al_2O_3 catalysts were therefore prepared from nickel acetate and their activity was studied in the hydrodesulfurization of dibenzothiophene. Separating the hypophosphite from the nickel compound has the advantage that the phosphate formed in the disproportionation of hypophosphite does not reach the Al_2O_3-supported Ni compound and cannot block the pores of the support. Ni_2P is formed by sequential reduction and phosphidation reactions and therefore its preparation demands careful adjustment of the synthesis conditions. Insufficient PH_3 leads to Ni and $Ni_{12}P_5$ side products and too much PH_3 to Ni_5P_4, which all have a lower HDS activity than Ni_2P.

1. Introduction

Metal sulfide catalysts are used in refineries to remove sulfur, nitrogen, and metals from oil fractions [1,2], but their catalytic activity is only moderate and catalysts with higher activity are highly desired. Metal-rich phosphides might be good hydrotreating catalysts because they often have metallic properties. Ni_2P and CoP, prepared by reduction of Ni and Co phosphates, were studied for the first time in hydrodenitrogenation (HDN) [3]. Other metal phosphides were prepared and tested in hydrodesulfurization (HDS), HDN, and hydrodeoxygenation (HDO) [4–6]. The properties of the active phase, the activation and deactivation, promoters, modified supports, and preparation conditions received attention [4–8] and temperature-programmed reduction (TPR) of a metal salt and phosphate was introduced as a convenient method to prepare transition-metal phosphides [9]. The HDS activity of several metal phosphides was found to be in the order of $Ni_2P > WP > MoP > CoP > Fe_2P$, with Ni_2P as the most active catalyst. However, unsupported Ni_2P catalysts have low surface area ($<1\ m^2/g$) and low activity. Therefore, metal phosphides have been put on supports such as silica (SiO_2) [5,10], γ-Al_2O_3 [11], active carbon [12], mesoporous MCM-41 [13] and SBA-15 [14], and molecular sieve MFI [15].

γ-Al_2O_3 is the most commonly used support for HDS catalysts, because it enables a high dispersion, is mechanically strong, has a good texture, can withstand water vapor that forms during regeneration of a catalyst, and is cheap. All these properties make γ-Al_2O_3 the preferred support in industry. However, the use of γ-Al_2O_3 as support for metal phosphides is not without difficulties [16–18]. The reason is that the reduction of phosphate is difficult and requires elevated temperature. Because of a strong interaction, phosphate and γ-Al_2O_3 react to form $AlPO_4$ at the high tempera-

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ture used in the TPR method. $AlPO_4$ cannot easily be reduced to phosphide and, as a consequence, a large part of the phosphate is unavailable for reduction to phosphide and excess phosphate has to be added to form metal phosphide particles on γ-Al_2O_3, leading to blocking of the pores of the support [16,18]. This is the key problem in the preparation of Ni_2P/γ-Al_2O_3 catalysts with high HDS performance. Only Ni2P/γ-Al_2O_3 with low dispersion can be obtained.

The P—O bond of oxy compounds with phosphorus in a lower valence state than P(V) is weaker than the P-O bond of phosphate and such compounds are easier to reduce. In past years, several studies have shown that phosphites (P(III)) [19–21] are easier to reduce and this made it possible to prepare Ni_2P at lower temperature. Hypophosphite, with the phosphorus atom in the P(I) state, is even easier to reduce than phosphite and bulk and supported metal phosphides have been prepared from metal salts and hypophosphite at a temperature as low as 200 °C [22–28]. Whereas phosphate and phosphite must be reduced with H_2 to make PH_3, which can reduce the nickel cations and form nickel phosphide, hypophosphite disproportionates to PH_3 and phosphate upon heating. The advantage of hypophosphite is that it disproportionates already at low temperature and that the interaction between phosphate and γ-Al_2O_3 can, thus, be kept low during the phosphidation of metal cations with PH_3. Its disadvantage is that phosphate is formed as coproduct, which is deposited on the support and causes pore blockage of the catalyst. In studies of supported metal phosphides [23,24,28], the phosphate and other salts were removed from the catalyst by thorough multi-step washing, but this makes catalyst preparation more difficult.

Recently, d'Aquino et al. and we have published methods to prepare Al_2O_3-supported Ni_2P from hypophosphite that avoid washing. d'Aquino et al. prepared Ni_2P/Al_2O_3 from nickel hypophosphite ($Ni(H_2PO_2)_2$), prepared by reacting nickel hydroxide with hypophosphorus acid [29]. Highly active Ni_2P on silica, alumina, and silica-alumina catalysts were obtained and the use of $Ni(OH)_2$ was claimed to obviate the need to wash away side products from the catalyst after preparation. We published a preliminary account of our efforts to avoid pore blockage by phosphate by separating the nickel source and hypophosphite source, so that only the gaseous PH_3, but not the phosphate, will reach the nickel [30]. An alternative method would be to use gas cylinders filled with PH_3, as used by Yang et al. [31]. The *in situ* generation of PH_3 is safer, however. In the present work we have extended the method of separating the nickel source and hypophosphite source. We studied the conditions for preparing Ni_2P with separate P and Ni sources with bulk samples. The optimum phosphiding conditions were then applied to the preparation of Ni_2P supported on alumina and the resulting catalysts were tested in the HDS reaction of dibenzothiophene.

2. Experimental methods

2.1. Preparation of Ni_2P and Ni_2P/Al_2O_3

Bulk Ni_2P samples were prepared using three phosphorus and five nickel sources. Hypophosphorous acid (H_3PO_2, 50 wt.% aqueous solution), NaH_2PO_2, and $NH_4H_2PO_2$ were used as P sources. As Ni sources, we used nickel nitrate, acetate, sulfate, and chloride, obtained by drying $Ni(NO_3)_2{\cdot}6H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, $NiSO_4{\cdot}6H_2O$, and $NiCl_2{\cdot}6H_2O$, respectively, at 120 °C for 12 h, as well as nickel oxide made by calcination of $Ni(NO_3)_2$ at 400 °C for 3 h. NaH_2PO_2 and $NH_4H_2PO_2$ were obtained from Aladdin and H_3PO_2 and all metal salts from Sinopharm Chemical Reagent Co., Ltd.

To phosphide the Ni compounds, the P and Ni sources were put in separate porcelain containers in a tubular reactor in a furnace. N_2 was flown through the reactor and the container with the P source was positioned upstream of the container with the Ni source (Fig. S1). The amount of PH_3 that is released by heating the phosphorus source and is used to phosphide the Ni compound depends on the temperature and N_2 gas flow rate, because part of the PH_3 will flow over the Ni compound without reaction. The unreacted PH3 in the exit gas was led through absorption bottles (MnO_2 first and then a NaOH solution), in which it reacts to a solution of sodium phosphate and phosphite. To optimize the P/Ni molar ratio for obtaining pure Ni_2P and to study the processes of transformation of Ni and P species, we varied the P/Ni molar ratio in the containers. The amount of the Ni source was kept constant at 0.25 g for all experiments and the amount of the P compound was varied, with molar P/Ni ratio between 2 and 6. The types and amounts of the precursors, the phosphidation conditions, and the products are listed in Table S1. The containers were heated in a 10 mL min^{-1} N_2 flow from room temperature to 120 °C at 2 °C min^{-1}, holding at 120 °C for 1 h to dehydrate the metal salt, further heating to 300 °C at 2 °C min^{-1}, and holding at 300 °C for 1 h. After cooling below 35 °C, the N_2 flow was terminated and the nickel phosphide was passivated in 10 vol% H_2S in H_2 (flowing with 10 mL min^{-1}) for 1 h. Usually, a low concentration of O_2 in inert gas is used to mildly oxidize the surface of Ni_2P to form a protective layer, but H_2S passivation proved to be superior to O_2 passivation for metal phosphides and give a higher HDS activity [32]. A study of Ni_2P/MCM-41 passivated by H_2S/H_2 showed that H_2S mainly reacted with the surface Ni sites, leaving the P sites almost unaffected. A covalent nickel phosphosulfide phase was formed during H_2S passivation, which was considered responsible for the high HDS activity [33].

Ni_2P/Al_2O_3 was prepared by incipient wetness impregnation of Al_2O_3 with an aqueous nickel salt solution. The Al_2O_3 (Shandong Alumina Plant) had a surface area of 147 m^2/g, a pore volume of 0.38 m^3/g, and an average pore diameter of 8.1 nm. Because the solubility of $Ni(CH_3COO)_2$ at room temperature is limited, the impregnation of Al_2O_3 with $Ni(CH_3COO)_2$ was performed at 60 °C so that a Ni loading of 10 wt% could be reached with one impregnation step. After impregnation, the sample was left overnight in air and dried at 120 °C for 12 h. The dried sample was pelletized, crushed, and sieved to 20–40 mesh size. The resulting particles were put in a porcelain container, the P source was put in another container, and both containers were placed in the furnace as described above. The PH_3 in the exit gas was led through absorption bottles (first MnO_2 and then a NaOH solution), in which it reacts to a solution of sodium phosphate and phosphite.

To compare our catalysts with catalysts made by co-impregnation, we prepared two catalysts by co-impregnating Al_2O_3 with a mixed solution of $Ni(CH_3COO)_2$ and H_3PO_2 at P/Ni = 3. After drying, the resulting material was heated in N_2 in a furnace at 300 °C. One portion of this catalyst was used as such; the other portion was washed several times with water to remove phosphate [23,24].

2.2. Characterization of Ni_2P and Ni_2P/Al_2O_3

The bulk Ni_2P and Ni_2P/Al_2O_3 samples were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption, thermogravimetry and differential scanning calorimetry (TG-DSC), transmission electron microscopy (TEM), temperature-programmed reduction in H_2 (H_2-TPR), field emission scanning electron microscopy (FESEM), CO chemisorption, and solid-state ^{31}P nuclear magnetic resonance (^{31}P NMR). Powder XRD patterns of the samples were measured on a PANalytical X'Pert PRO diffractometer with Cu $K\alpha$ monochromatized radiation (λ = 1.54 Å) operated at 45 kV and 40 mA, with a scan rate of 8° per min and a 2θ scan range from 5° to 75°. N_2 adsorption-desorption measurements were carried out on a Tristar II 3020 analyzer at −196 °C. Samples were outgassed overnight at 300 °C

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