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Essential elucidation for preparation of supported nickel phosphide upon nickel phosphate precursor

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ABSTRACT

Preparation of supported nickel phosphide (Ni_2P) depends on nickel phosphate precursor, generally related to its chemical composition and supports. Study of this dependence is essential and meaningful for the preparation of supported Ni_2P with excellent catalytic activity. The chemical nature of nickel phosphate precursor is revealed by Raman and UV–vis spectra. It is found that initial P/Ni mole ratio ≥ 0.8 prohibits the Ni–O–Ni bridge bonding (*i.e.*, nickel oxide). This chemical bonding will not result in Ni_2P structure, verified by XRD characterization results. The alumina (namely, $\gamma\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, or $\alpha\text{-Al}_2\text{O}_3$) with distinct physiochemical properties also results in diverse chemical nature of nickel phosphate, and then different nickel phosphides. The influence of alumina support on producing Ni_2P was explained by the theory of surface energy heterogeneity, calculated by the NLDFT method based on N_2 -sorption isotherm. The uniform surface energy of $\alpha\text{-Al}_2\text{O}_3$ results only in the nickel phosphosate precursor and thus the Ni_2P phase.

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1. Introduction

In recent years, nickel phosphide (Ni_2P) supported on SiO_2 , Al_2O_3 , or zeolite *etc.*, has been found to be capable of catalyzing hydrotreatment [1–3]. It exhibits superior activity to those of commercial transition metal sulfide catalysts [4,5]. Its superior activity stimulates an urge to develop a reliable preparation process for supported Ni_2P as an industrial catalyst. A temperature-programmed reduction (TPR) method is practical, and commonly used to reduce nickel phosphate precursor to nickel phosphide. The major drawback of this preparation method is related to high temperature above 823 K [6]. This drawback can be overcome by catalytic effects of noble metals, whereby actual preparation temperature can be lowered to below 773 K [7,8]. The improved method is suggested as a catalyzed preparation. Pd catalyzed preparation of supported Ni_2P , as well as the conventional TPR preparation, is significantly influenced by many factors, such as initial P/Ni mole ratio [9,10], support type [11], Ni loading [12], and gas hourly space velocity of reduction agent [13]. Such an influence is worth elucidating for producing the most stable Ni_2P with excellent intrinsic activity [14,15].

Among those factors, the initial P/Ni mole ratio and support type determine the feasibility for the preparation of supported

Ni_2P . Typically, Ni_2P is reduced only from nickel phosphate precursor with certain initial P/Ni mole ratio ≥ 0.8 [16], obeying the solid transformation mechanism [6]. Initial P/Ni mole ratio up to 2.0 is adopted for producing $\gamma\text{-Al}_2\text{O}_3$ supported Ni_2P ($\text{Ni}_2\text{P}/\gamma\text{-Al}_2\text{O}_3$) [17]. These actual values are higher than the stoichiometry (0.5) of Ni_2P . Such a gap of P/Ni mole ratio leads to excess phosphorous (P). Current view about this gap is that the excess P is necessary to compensate P loss as volatile P species, during reduction at high temperatures. Another possible reason is the strong interaction between the phosphate ions and support. For instance, the phosphate interacts with $\gamma\text{-Al}_2\text{O}_3$ support to form AlPO_4 that will not be reduced to phosphide [18]. To avoid this high temperature reduction, a feasible strategy is to adopt an inert support, such as $\alpha\text{-Al}_2\text{O}_3$. The aforementioned strong interaction will also be prevented for the inert $\alpha\text{-Al}_2\text{O}_3$, which weakly interacts with its nickel phosphate precursor, even as a supporting active phase. It is thus beneficial to significantly promote catalytic performance, despite its poor surface area [19]. One issue of this strategy is the required initial P/Ni mole ratio for catalyzed preparation of Ni_2P supported on inert $\alpha\text{-Al}_2\text{O}_3$ (denoted as $\text{Ni}_2\text{P}/\alpha\text{-Al}_2\text{O}_3$).

Another focus is how the preparation of supported Ni_2P depends on its precursor with diverse chemical nature and varying initial P/Ni mole ratio. This will be investigated by Raman and UV–vis spectra. Besides the initial P/Ni mole ratio, choosing the supports with different surface properties can result in distinct chemical natures and reducibilities of the precursors. The chemical nature indeed makes up the reducibility of the precursor, shown

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by H₂-TPR characterization [11]. Hence, it is worth associating the chemical nature with reducibility of nickel phosphate precursor. Among conventional supports, alumina (namely, γ -Al₂O₃, θ -Al₂O₃, or α -Al₂O₃) is recognized as an important hydrotreating catalysts support [20], and deserves to be thoroughly scrutinized. We will tentatively explain the α -Al₂O₃ as the preferred support for Ni₂P rather than γ -Al₂O₃ and θ -Al₂O₃, from a theoretical viewpoint of surface energy heterogeneity. For an ideal uniformity of a structure, real solid surfaces of those supports are rarely approached [21]. Such surface energy heterogeneity will critically govern the preparation of supported phase and activity [22]. To our best knowledge, surface energy heterogeneity has not yet been adopted to interpret the influence of support type on preparing nickel phosphide. It is also meaningful to essentially elucidate the preparation of supported nickel phosphide depending on nickel phosphate precursor.

2. Experimental

2.1. Materials

Nickel nitrate hexhydrate [Ni(NO₃)₂·6H₂O, 98.5%] and ammonium dihydrogen phosphate (NH₄H₂PO₄, 99.0%) were supplied by Sinopharm Chemical Reagent Co. Ltd. Palladium chloride (PdCl₂, 99%) was purchased from Sino Platinum Metals Co. Commercial γ -Al₂O₃ (A-AS-04 type, 2–3 mm) was purchased from Aluminum Corporation of China, Ltd. (Shandong Branch). The purchased γ -Al₂O₃ was calcinated at 1123 K for 5 h before use. θ -Al₂O₃ and α -Al₂O₃ were obtained by calcinating the γ -Al₂O₃ at 1273 and 1473 K for 5 h, respectively.

2.2. Catalyzed preparation of supported nickel phosphide

Based on our previous work [8], alumina (namely, γ -Al₂O₃, θ -Al₂O₃, or α -Al₂O₃) supported nickel phosphides were prepared via the temperature-programmed reduction (TPR) method consisting of incipient impregnation, drying, calcination, and reduction. Typical preparation procedures are described as follows. One Al₂O₃ support (pore volume=0.6 cm³/g) was incipient co-impregnated with a mixture solution of Ni(NO₃)₂·6H₂O, NH₄H₂PO₄, and PdCl₂. The [Ni²⁺] of that mixture solution was adjusted to be 2.0, 2.5, or 3.0 mol/L, corresponding to Ni loading ($W_{\text{Ni}}/(W_{\text{Ni}}+W_{\text{Al}_2\text{O}_3}) \times 100\%$) of 10, 12, or 15 wt% in the final samples, respectively. PdCl₂ was dissolved by adding an appreciate amount of HCl, with the consequent [Pd²⁺] being 0.005 or 0.01 mol/L. The corresponding Pd contents ($W_{\text{Pd}}/W_{\text{Al}_2\text{O}_3} \times 100\%$) were calculated to be ca. 0.05–0.1 wt%. The P/Ni mole ratio in that mixture solution varied from 0.4 to 1.4. Those samples were dried at 333 K for 6 h, followed by calcination at 673 K for 3 h. The resulting samples were incipient re-impregnated with the above mixture solution, followed by drying and calcination. The obtained amorphous oxidic precursors [23] were temperature-programmed reduced to nickel phosphides. In a typical experiment, 15 mL samples were loaded into a stainless tube reactor (*I.D.*=22 mm), placed in a furnace controlled by a temperature programmer-controller. The reduction was carried out in a flow of H₂ (99.5 v%) at 20, 200, or 600 h⁻¹ (*S.T.P.*, GHSV), while the temperature was raised from room temperature to 673 K at 2 K/min, and then to 768 K at 0.25 K/min, holding at that final temperature for 3 h.

The reduced samples were denoted as wNiP_xPd_y/ γ , θ , α -Al₂O₃-z, where *w* is the Ni loading \times 100, subscript *x* is the P/Ni mole ratio, *y* is the Pd content multiplied by 10,000, and *z* is the GHSV of H₂. The corresponding oxidic precursors are labeled as wNiP_xOPd_y/ γ , θ , α -Al₂O₃. For example, 10NiP_{1.0}Pd5/ α -Al₂O₃-200 refers to the sample reduced from α -Al₂O₃ supported nickel phosphate oxidic

precursor with an initial P/Ni mole ratio of 1.0 in a 200 h⁻¹H₂ flow, in which Ni loading and Pd content are 10 wt% and 0.05 wt%, respectively. An Ni₂P yield of the reduced samples, hereinafter, is defined as the Ni₂P weight content in the generated phases, analyzed via XRD characterization. The Ni₂P yield of 100 wt% corresponds to the generation of pure Ni₂P phase.

2.3. Characterization

2.3.1. XRD

Powder XRD patterns were collected within a range of $2\theta=20\text{--}70^\circ$ on a Rigaku D-max2500v/pc X-ray diffractometer equipped with Cu-K α radiation. The step size used was 0.02° (step time 1.0 s). The collected data can reveal crystal phases of nickel phosphides, namely, Ni₂P, Ni₁₂P₅, or Ni₃P, referring to PDF65-1605, 65-1623, or 65-1989, respectively. Their crystal sizes were estimated by the Scherrer equation based on the feature XRD peaks due to Ni₂P(111), Ni₁₂P₅(312), or Ni₃P(321), correspondingly. The Ni₂P weight content in the generated phases was calculated by a RIR method through an MDI Jade 5.0 program.

2.3.2. H₂-TPR

H₂-temperature programmed reduction (H₂-TPR) experiment was performed on an AutoChem 2920 (Micromeritics). Samples of weight 50 ± 5 mg were loaded in an U type reactor, and heated to 1123 K with a ramp of 5 K/min in a 50 mL/min H₂/Ar (10 v%) flow.

2.3.3. FT-IR, UV-vis, and Raman spectrum analysis

IR spectra with a resolution of 4 cm⁻¹ were scanned (5 scans) at room temperature on a Nicolet 6700 FT-IR spectrophotometer. The samples were finely ground and dispersed in KBr pellets with a ratio of about 5 mg per 100 mg of KBr. Ultraviolet-visible diffuse reflectance spectra (DRS) of samples were obtained at room temperature on a Hitache U-4100 spectrophotometer. Data were collected by linear scanning over a range of 200–800 nm. All samples were ground before measuring, and α -Al₂O₃ was used as the reflectance reference. Raman spectra of the samples were obtained on an inVia Raman microscope (Renishaw) equipped with 532 nm line of the laser under ambient conditions.

2.3.4. N₂-physical absorption and mercury porosimetry

Nitrogen adsorption measurements were carried out to reveal micro/mesoporous structure at 77 K on an AutoChem 2020 Analyzer (Micromeritics). Before analysis, samples were dried at 473 K for 3 h in N₂ (99.999%) atmosphere. The surface area was calculated using a BET method on the basis of adsorption branch in a 0.05–0.30 partial pressure range. The total pore volume was determined from the amount of N₂ adsorbed at a relative pressure $P/P_0=0.99$ by assuming that all the accessible pores were filled by liquid nitrogen. The BET surface areas were compared with the results obtained by a Non-Local Density Functional Theory (NLDFT) method. This method was also used to reveal the pore size and surface energy distribution. Mercury porosimetry was utilized to study macroporous structure on an AutoPore IV 9500 Analyzer (Micromeritics).

2.4. EDX

Elemental composition was analyzed by Energy-Dispersive X-ray spectroscopy (EDX) on an INCA energy apparatus (Oxford Instruments).

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