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Synthesis of high-dispersed $NiCoP/SiO_2$ and hydrodesulfurization performance

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ABSTRACT

Supported bimetal phosphide ($NiCoP/SiO_2$) catalysts with variable Ni/Co mole ratios at low temperature were synthesized by a novel route using sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), nickel acetate ($Ni(AC)_2 \cdot 4H_2O$) and cobalt acetate ($Co(AC)_2 \cdot 4H_2O$) as materials. The structure, composition and properties of the as-prepared catalysts were characterized by X-ray diffraction, inductively coupled plasma atomic emission spectroscopy, high resolution transmission electron microscope, Fourier transform infrared spectroscopy, N_2 adsorption measurement, thermogravimetric analyzer and gas chromatograph-mass spectrometer. The transmission electron microscope analysis showed the as-obtained NiCoP nanoparticles were highly dispersed on the SiO_2 support. The hydrodesulfurization conversion reached 73.7% over the as-synthesized $NiCoP/SiO_2$ (Ni: 10 wt.%, Co: 10 wt.%), which resulted from the highly disperse NiCoP active phase on the SiO_2 support. In addition, the preparation mechanism and desulfurization path were also discussed in detail.

Recently, the fog and haze in air is aggravating, with an amount of haze originating from the photochemical reaction of sulfur compounds in the automobile exhaust, which can be circumvented by removing sulfur compounds from gasoline and diesel in the refining industry [1]. Therefore, it is necessary to develop a cheap, efficient and stable desulphurization catalyst. Of the metal phosphides with high hydrodesulfurization (HDS) activity and stability [2,3], bimetal phosphides, such as Ni_xMo_yP [4,5], Co_xMo_yP [6,7], Ni_xCo_yP [8,9], Ni_xFe_yP [10], are excellent desulphurization catalysts. In this study, we report a new method to prepare highly dispersed NiCoP catalysts at 350 °C. During preparation, we first impregnated $Ni(AC)_2 \cdot 4H_2O$ and $Co(AC)_2 \cdot 4H_2O$ on the SiO_2 carrier, and then calcined the coated SiO_2 carrier to produce and to allow nickel oxide (NiO) and cobalt oxide (CoO) highly dispersed on the SiO_2 support. Finally, NiO and CoO over the SiO_2 support were reduced by phosphine (PH_3) to produce a highly dispersed $NiCoP/SiO_2$ catalyst. The activity measurement of the as-obtained $NiCoP/SiO_2$ catalyst showed that it had a good desulfurization performance.

In a typical experiment, 2.54 g $Ni(AC)_2 \cdot 4H_2O$ and 2.54 g $Co(AC)_2 \cdot 4H_2O$ were dissolved in 50 mL of deionized water. 4.8 g SiO_2 (479 m^2/g, 15 nm) was added to the above solution under stirring. The SiO_2 support was impregnated in the above solution for 3 h. The mixture was filtered and dried at 120 °C for 3 h. The pulverized powder was calcined in a muffle furnace at 500 °C for 3 h to produce SiO_2 supported NiO and CoO. 0.8 g precursor and 0.82 g $NaH_2PO_2 \cdot H_2O$ (the molar ratio of Ni/Co/P = 1:1:6) were mixed under grinding. The above mixture was heated to 350 °C for 1 h in a home-made tube furnace in a flowing N_2 (30 mL/min, 1 atm). Finally, the obtained sample was grinded to powder (20–40 mesh). Samples with a range of Ni/Co ratios were prepared by changing the molar ratio of Ni/Co (Ni/Co = 4:6, 3:7, 2:8, 6:4, 7:3, 8:2) in the $NiO + CoO/SiO_2$ precursor (Ni + Co: 20 wt.%). In the process of preparing metal phosphides, the molar ratio of Ni + Co/P remained 2:6. The Ni_2P/SiO_2 (Ni: 10 wt.%) was synthesized under the same conditions without Co^{2+} ions.

X-ray diffraction (XRD) patterns of the samples were performed on the X-ray diffractometer (Rigaku D/max 2500) with Cu-Kα radiation (λ = 1.5406Å) in the range of 2θ = 10–80°. The element compositions of the samples were analyzed by inductively coupled

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plasma atomic emission spectroscopy (ICP-AES, Varian 715-ES). The shape and size of the samples were observed by a high resolution transmission electron microscope (HRTEM, JEM 2010, 200 kV). Fourier transform infrared (FT-IR) spectra of the samples were done by a Tensor37 Bruker infrared spectrometer. The Brunauer-Emmett-Teller (BET) surface area of the samples was measured by a Micromeritics ASAP2020 automatic surface area analyzer. Thermogravimetric analysis (TG) of the samples was characterized on a PerkinElmer simultaneous thermal analyzer (N_2, 15 °C/min). The products were analyzed by an Agilent 7890A/5975C gas chromatograph-mass spectrometer (GC-MS).

The hydrodesulfurization (HDS) ability measure for dibenzothiophene (DBT) was done in a home-made tubular reactor at 320 °C and a total pressure of 3.0 MPa 1 mL of 20–40 mesh NiCoP/SiO_2 catalyst (0.6 g) was mixed with 4.0 mL 20–40 mesh quartz sands. The mixture was reduced at 400 °C for 3 h in a 200 mL/min H_2 flow. The temperature was decreased to 320 °C after reducing. And then 0.5 wt.% of DBT decalin solution was were pumped into the reactor at 9 mL/h. The reaction products were analyzed off-line by an gas chromatograph equipped with a OV101 column and a flame ionization detector (FID).

Fig. 1 shows the XRD patterns of the as-prepared sample. The peaks at 40.99°, 44.90°, 47.58°, 54.44°, and 75.41° are assigned to the (1 1 1), (2 0 1), (2 1 0), (3 0 0), (212) planes of hexagonal NiCoP phase (JCPDS cards no. 71-2336). No other diffraction peaks were discerned. Therefore, pure NiCoP has formed in our experimental condition. The peak at about 22° is assigned to the SiO_2 support. In comparison with the SiO_2 peak, the peak intensity of NiCoP was moderate, indicating that the active phase of NiCoP was well dispersed on the carrier surface of SiO_2.

Fig. 2 shows the HRTEM image of NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%). Fig. 2(a) is a low-magnification image of NiCoP/SiO_2, in which the gray particles are the SiO_2 support (about 15 nm in diameter) and the black particles are active NiCoP particles. The NiCoP particles are closely supported on the SiO_2 surface. The tiny NiCoP particles congregate (<10 nm in diameter) due to the calcined precursor. Fig. 2(b) is a high-magnification image of NiCoP/SiO_2. The diameter of the NiCoP particle that is surrounded by the SiO_2 support (amorphous region) is about 7.5 nm. A light gray band with a thickness of approximately 0.22 nm extends around the external edge of the NiCoP particle, being consistent with the d-spacing value for {111} crystallographic planes of the NiCoP phase. The corresponding selected area electron diffraction (SAED) pattern (Fig. 2(c)) suggests

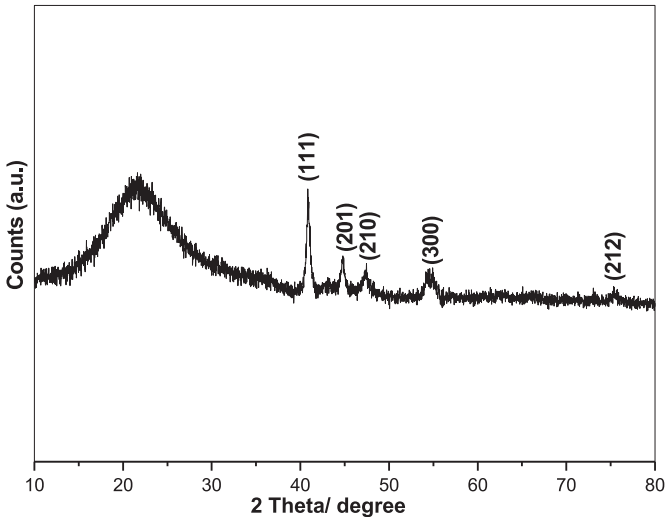

Fig. 1. X-ray diffraction patterns of NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) prepared at 350 °C for 1 h.

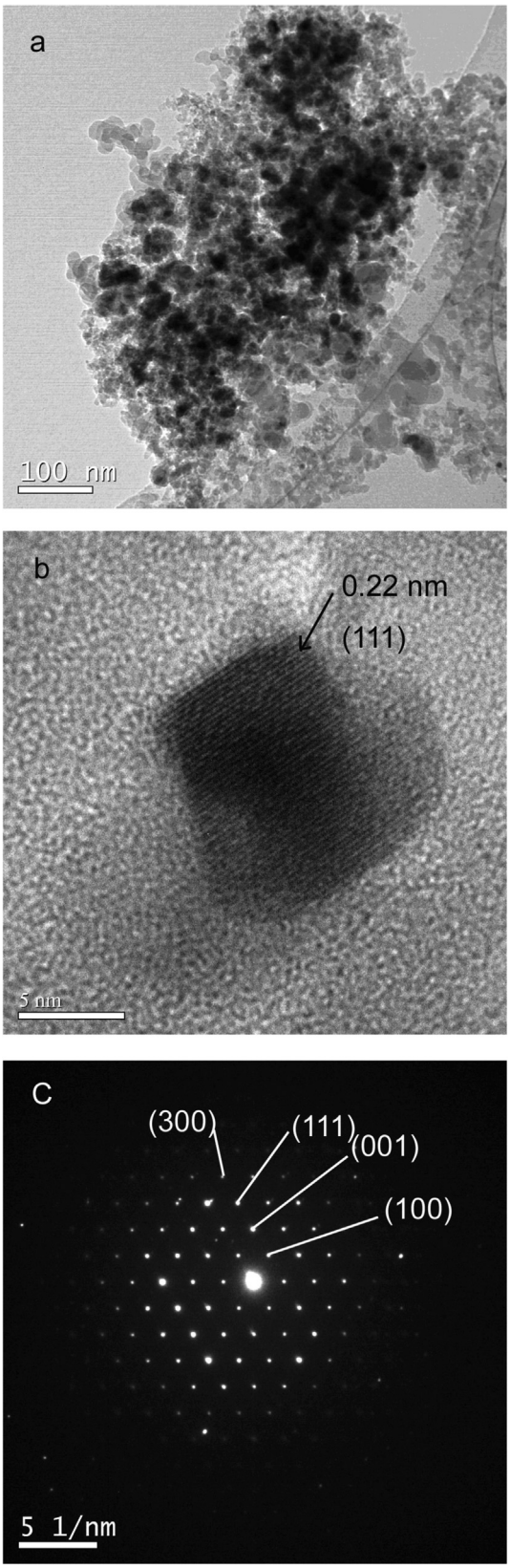

Fig. 2. HRTEM images of the NiCoP/SiO_2 (Ni: 10 wt.%, Co: 10 wt.%) prepared at 350 °C for 1 h.