Support information

The selective cleavage of C–O linkages and efficient hydrogenation over cobalt-doped nickel phosphide catalyst

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Materials

Nickell(II) chloride hexahydrate ($NiCl_2·6H_2O$, 98%), ethylene glycol ($C_2H_6O_2$, 98%), and n-hexane (C_6H_{14}, 98%) were purchased from Tianjin Xinbote Chemical Co., Ltd. Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, ≥99%) was supplied by Tianjin Zhiyuan Chemical Reagent Co., Ltd. Sodium hypophosphite monohydrate ($NaH_2PO_2·H_2O$, 99%) and phenyl benzyl ether ($C_{13}H_{12}O$, >98%) were obtained from Aladdin Biochemical Technology Co., Ltd. All chemicals and reagents were used as received without further purification.

Catalyst preparation

In this experiment, $Ni_{12}P_5$ served as the reference catalyst. The catalyst was synthesized using a straightforward one-step solvothermal method. First, 1.43 g (6 mmol) of $NiCl_2·6H_2O$ and 4.4516 g (42 mmol) of $NaH_2PO_2·H_2O$ were dissolved in 60 mL of ethylene glycol solvent. The solution was stirred for 6 h, then transferred to a Teflon-lined autoclave, where it was heated at 180 °C for 12 h. After the reaction, the solution was cooled to room temperature, then washed and filtered. The product was dried in an oven at 60 °C to yield the black $Ni_{12}P_5$. The preparation of Co-$Ni_{12}P_5$ followed a similar process, except that the cobalt source ratio was varied. Co-$Ni_{12}P_5$with cobalt concentrations of 1%, 3%, 5%, and 10% were synthesized and labeled as 1% Co-$Ni_{12}P_5$, 3% Co-$Ni_{12}P_5$, 5% Co-$Ni_{12}P_5$, and 10% Co-$Ni_{12}P_5$, respectively. The detailed preparation process is illustrated in Figure S1.

Characterizations

The phase composition of the synthesized catalyst was analyzed using a Bruker D8 X-ray diffractometer (XRD, Germany). The analysis was conducted within a scanning angle of 10° to 80°, utilizing a Cu-Kα radiation source and a scanning voltage of 40 kV to determine the crystal structure of the catalyst. The morphology of the catalyst was observed with a Hitachi SU-4800 scanning electron microscope (SEM, Japan). The chemical states of the catalyst were examined using a Thermo Scientific NexsaG2 X-ray photoelectron spectrometer (XPS) with a monochromatic Al target as the X-ray source, covering an energy range of 0 eV to 1486.6 eV. The microstructure was analyzed using a Tecnai F20 high-resolution transmission electron microscope (TEM, FEI, USA). The morphology was further analyzed using a JEM-2100F high-resolution field emission transmission electron microscope (HRTEM). The acidity of the catalyst was measured by ammonia temperature-programmed desorption (NH_3-TPD) using a BELCAT instrument (Japan). Before ammonia adsorption, 0.1 g of the catalyst was pretreated under a helium flow at 450 ℃ for 1 h, then cooled to 100 ℃. The temperature was subsequently raised from 100 ℃ to 500 ℃ at a rate of 10 ℃/min under a helium flow rate of 20 mL/min for ammonia desorption. The BET surface area was determined using the Brunauer-Emmett-Teller (BET) equation, and micropore properties were analyzed using the t-plot method. Pore size was calculated with the Barrett-Joyner-Halenda (BJH) equation from the N_2 adsorption-desorption isotherm, and total pore volume was obtained from the N_2 volume adsorbed at a relative pressure of 0.99. Pyridine Infrared Spectroscopy (Py-IR) spectra were recorded on a Bruker Invenio-S instrument equipped with an in-situ cell. Self-supported wafers (30 mg) of the samples were degassed at 350℃ for 1 h under dynamic vacuum (<10^{-6} Pa). After activation, the base spectrum was recorded, and then pyridine vapor was carried into the cell via a bubbler and adsorbed on the samples. Desorption of pyridine was performed under vacuum at 30℃ and afterwards cooled to 250℃ to collect IR spectra. The content of Co, Ni, and P was determined on a PerkinElmer Optima 8000 spectrometer exploiting Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

DFT calculation

DFT calculations were conducted using VASP (Vienna Ab-initio Simulation Package) version 5.4. The PAW (Projector Augmented Wave) pseudopotential and the PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional were employed, with a plane wave cutoff energy of 500 eV. A real-space distance of at least 15 Å was maintained for all periodic slab calculations. A 3×3×1 k-point grid was applied to calculate the pristine $Ni_{12}P_5$ and 3% Co-NiFeCeP systems. Convergence criteria were set to 10^{-5} eV for energy and 0.05 eV/Å for force. Spin polarization was included in all structure calculations. The DFT-D3 method was used to account for van der Waals interactions. The adsorption energy (Eads) was computed using the following equation:

$E_{ads}=E_{total}-(E_{catalyst}+E_{adsorbate})$

Where E_{total} was the total energy of the catalyst and adsorbate, and $E_{catalyst}$ and $E_{adsorbate}$ were the energies of the catalyst and adsorbate, respectively.

Catalysis

The catalytic hydrogenation of BPE was carried out by adding 100 mg of BPE, 50 mg of catalyst, and 20 mL of n-hexane to a 50 mL high-pressure reactor. The reactor was first purged three times with nitrogen (N_2) and checked for leaks to ensure it was properly sealed. Following this, the reactor was purged three times with hydrogen (H_2), and hydrogen was then introduced at pressures of 0.5 MPa, 1 MPa, 1.5 MPa, 2

MPa, and 2.5 MPa. The reactor was heated to the desired reaction temperature and maintained for 0.5 h, 1 h, 1.5 h, 2 h, and 2.5 h. After the reaction, the reactor was cooled to room temperature, and the liquid product was separated from the catalyst by filtration using a Buchner funnel. The liquid product was collected and analyzed with an Agilent 5977B GC-MS system (Agilent, USA). The analysis was conducted using an HP-5 capillary column (60 m × 250 μm × 0.25μm). The initial column temperature is set to 60 ℃ and increased at a rate of 5 ℃/min to 250 ℃, where it was held for 10 minutes. Mass spectrometry was performed using electron ionization (EI) with a split ratio of 20:1, and the scan range was from m/z 35 to 550.

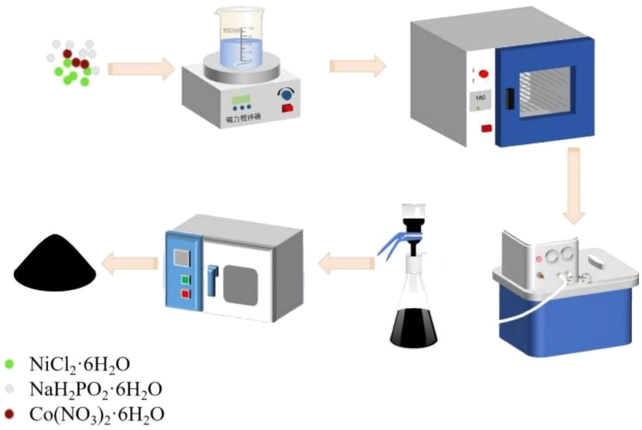

Figure S1. Schematic diagram illustrating the synthesis of x% Co-$Ni_{12}P_5$.

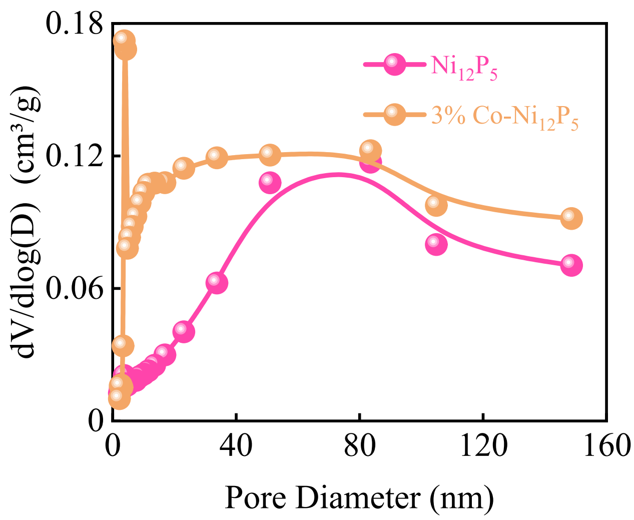

Figure S2. Pore size distribution of $Ni_{12}P_5$ and 3% Co-$Ni_{12}P_5$.

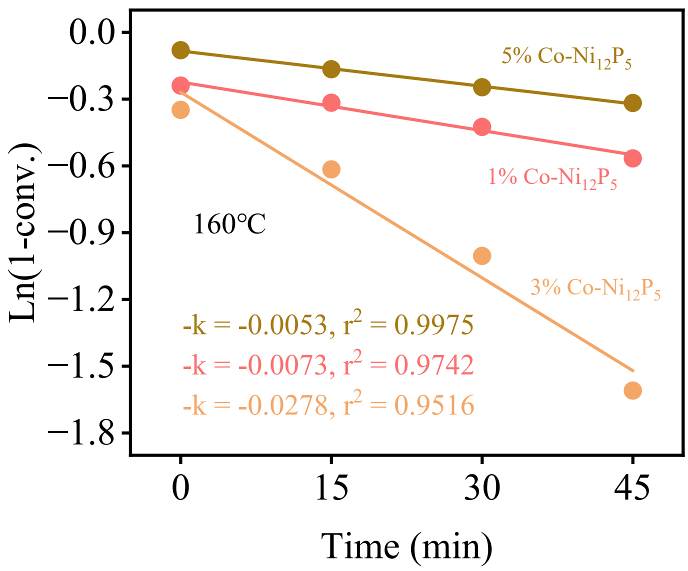

Figure S3. Pseudo-first-order kinetic fitting at different cobalt contents (100 mg BPE, 20 mL n-hexane, 50 mg x% Co-$Ni_{12}P_5$, 160 °C, 1.5 MPa H_2).

Table S1 The specific surface area and porosity of $Ni_{12}P_5$ and 3% Co-$Ni_{12}P_5$

Sample	S_{BET}(m^2/g)	D_{pore}(nm)	V_{total}(cm^3/g)	[a]particle size(nm)
$Ni_{12}P_5$	18.28	21.44	0.10	23.94
3% Co-$Ni_{12}P_5$	52.79	14.49	0.02	11.28

a： Measured by TEM

Table S2 Acid amounts of $Ni_{12}P_5$ and 3% Co-$Ni_{12}P_5$

Sample	Acidity (mmol NH_3 g^{-1})			Total (mmol NH_3 g^{-1})
	Weak acid（<230 ℃）		Moderately acid (230-500 ℃)	
$Ni_{12}P_5$	36.84	42.12	21.04	100
	0.07	0.08	0.04	0.19
3% Co-$Ni_{12}P_5$	56.41	15.38	28.21	100
	0.22	0.06	0.11	0.39

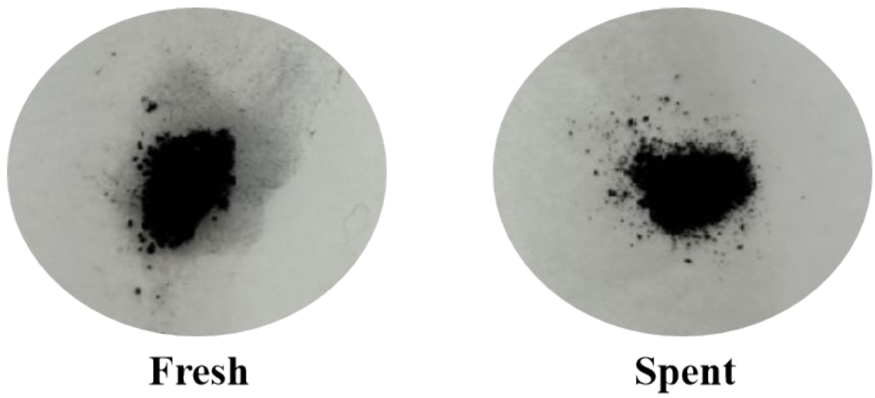

Figure S4. Color comparison of 3% Co- $Ni_{12}P_5$ before and after reaction.

Table S3 ICP analysis of the reaction filtrate for Co, Ni, and P leaching from 3% Co-$Ni_{12}P_5$ after catalytic hydrogenation

Sample	P (ug/g)	Co (ug/g)	Ni (ug/g)
3% Co-$Ni_{12}P_5$	-	0.005	0.224