Supporting Information

Microwave assisted combustion of phytic acid for preparation of

Ni₂P@C as robust catalyst for hydrodechlorination

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Experimental

Preparation of Catalysts

For the preparation of Ni₂P catalysts (with molar ratio of Ni:P=1:2.5 as the example), 3.7 g Ni(NO₃)₂.6H₂O (98%, Aladdin Industrial Corporation, Shanghai, China) and 11 g C₆H₁₈O₂₄P₆ (phytic acid, 50%, Aladdin Industrial Corporation, Shanghai, China) were well mixed in a beaker. Following stirring for 2 hours drying at 120 °C in an oven, gelatinous paste was obtained. The paste underwent combustion in the home domestic microwave oven for 3 min with high heat (700 W), resulting in 5.14 g fluffy substance. The precursor was obtained by granulating the shaggy material and collecting 20-40 mesh particles. Ultimately, the precursor were reduced in H₂ flow (99.999%, 100 ml/min) for 3 h. The reduction temperature was increased from room temperature to 923K with a ramp rate of 5 K/min, and finally 2.31 g fresh catalyst was obtained.

For comparison, Pd/C and Ni/C were also prepared. $PdCI_2$ (59-60%, Aladdin Industrial Corporation, Shanghai, China) was dissolved in water and stirred for 2 hours. Then the solution was immersed on activated carbon in equal volume

for 12 hours. Then it was dried in an oven at $80^\circ C$ to obtain the precursor.

Catalysts were obtained by reducing precursors in hydrogen atmosphere for 3

hours at 300° C.

 $Ni(NO_3)_2 \cdot 6H_2O(98\%)$, Aladdin Industrial Corporation, Shanghai, China was dissolved and stirred for 2 hours. Phytic acid was placed in microwave oven and burned for 3 minutes at 700 W high temperature to obtain black solid. $Ni(NO_3)_2 \cdot .6H_2O$ was impregnated on black solid for 12 hours, then dried in 80 degree oven to obtain precursor. Catalysts were obtained by reducing precursors

at 650℃ for 3 hours in hydrogen atmosphere.

Catalyst characterization

The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Kratos AXIS Ultra DLD analytical instrument. A monochromatic Al K radiation source (1486.6 eV) with an analyzer pass energy of 80 eV was operated at 3 mA and 15 kV. The scanning rate was set to 5° /min.

The surface area and total pore volume of the catalysts were measured by N_2 adsorption–desorption at -196 °C at 77K on a Micromeretics ASAP 2020 instrument in static measurement mode. Prior to the measurement, the catalyst samples were degassed at 473K for 12h.

The acidity of the catalysts was evaluated by ammonia temperature-programmed desorption (NH₃-TPD), which was carried out in a fixed-bed reactor containing 50mg of catalyst. The sample was heated in a flow of He to 573K at a rate of 10K/min, and kept at 573K for 1h. After cooling down to 373K, the sample was heated from 373 K to 1123 K with a heating rate of 10K/min in He atmosphere. The NH₃ desorption amount was measured by a gas chromatograph with a thermal conductivity detector (TCD).

For the morphology investigation, SEM (scanning electron microscope) images were captured on a scanning electron microscope (FESEM, Hitachi S4700) at an accelerating voltage of 15kV equipped with an X-ray energy spectrometer (EDS).

The X-ray photoelectron spectroscopy (XPS) measurements of the catalysts were performed by Thermo ESCALAB 250XI, equipped with monochromatised Al K α X-ray as the excitation source (24.2W), with an analyzer pass energy of 187.85 eV for survey scans and 46.95 eV for detailed elemental scans. In order to subtract the surface charging effect, binding energies were referenced to C1s binding energy of carbon, taken to be 284.8 eV. The XPS spectra were analyzed by the XPS peak software.

TEM (transmission electron microscopy) was adopted to further explore the microstructure of the catalysts using a JEOL 2100F transmission electron microscope at an accelerating voltage of 200 kV.

Catalytic activity evaluation

The catalytic experiments were carried out over the fixed bed reactor (stainless steel, 8 mm (i.d)*400 mm) with atmospheric pressure. A thermalcouple was placed in the middle of the catalyst bed to detect the actual reaction temperature. Before catalytic reactions, 4 ml of the catalyst (20-40 mesh) was loaded into the isothermal zone of the reactor. Then the feed gases including chlorodifluoromethane (HCFC-22, 8 mL/min), N₂ (16 mL/min) and H₂ (8 mL/min) controlled by mass flowrate controllers respectively were introduced to the reactor. The reaction temperature was maintained at 400 °C, 450 °C and 500 °C, respectively. The products formed during the reaction were passed through a KOH solution to trap HCl, and then the gaseous products were analyzed by an online gas chromatograph (Fuli GC9790) equipped with a PoraPLOT Q column and a TCD (thermal conductivity detector).



20 (°) Figure S1 XRD pattern of phytic acid and nickel nitrate mixture following drying at 120 °C (without combustion). Ni₂P₄O₁₂-like structure is identified indicating the interaction of phytic acid with Ni²⁺ in the solution.



Figure S2 XRD pattern of as-prepared catalyst (without reduction) following microwave assisted combustion of phytic acid and nickel nitrate.



Figure S3 EDS mapping analysis of fresh Ni_2P catalyst prepared by microwave assisted combustion of phytic acid and nickel nitrate and reduced at 650 °C for 3 h in H₂ atmosphere.

Catalyst	Elemental concentration (mol%)			
	Ni	Р	0	С
Fresh	7.02	16.07	47.08	29.83
Spent	2.96	4.31	16.35	76.39

Table S1 Elemental content analysis by XPS for the fresh and spent catalyst.



Figure S4 SEM image of sample prepared by microwave assisted combustion of phytic acid and nickel nitrate (without reduction).



Figure S5 EDX mapping of fresh Ni_2P catalyst prepared by microwave assisted combustion of phytic acid and nickel nitrate and reduced at 650 °C for 3 h in H₂ atmosphere.



Figure S6 TEM images Ni_2P catalyst prepared by microwave assisted combustion of phytic acid and nickel nitrate and reduced at 650 °C for 3 h in H₂ atmosphere.



Figure S7 N₂ adsorption–desorption isotherms of Ni₂P catalyst prepared by microwave assisted combustion of phytic acid and nickel nitrate and reduced at 650 °C for 3 h in H₂ atmosphere.



Figure S8 Selectivity to CHF₃ (HFC-23) during catalytic hydrodechlorination of HCFC-22 over Ni₂P@C, Ni/C and Pd/C at 450 °C, atmospheric pressure and GHSV (gas hourly space velocity) of 480 h⁻¹.



Figure S9 NH₃-TPD-MS spectrum of Ni₂P@C. (a) Fresh catalyst and (b) spent catalyst. NH₃ during desorption was monitored by a mass spectrometer with the detection m/e of 17.



Figure S10 TEM image of spent Ni₂P@C catalyst.



Figure S11 XRD patterns of fresh and spent Ni₂P@C catalyst.



Figure S12 Effect of reduction time on the catalytic performance of Ni₂P@C for the hydrodechlorination of HCFC-22 at 450 °C, atmospheric pressure and GHSV (gas hourly space velocity) of 480 h⁻¹. (a) Conversion of HCFC-22 as a function of TOS. (b) Selectivity to CH_2F_2 (HFC-32) as a function of TOS. (c) Selectivity to CHF_3 (HFC-23) as a function of TOS.



Figure S13 XRD pattern of catalyst following reduction at 650 °C for 6 h.



Figure S14 High-resolution Ni 2p XPS spectrum of catalyst following reduction at 650 °C for 6 h..



Figure S15 Effect of Ni/P molar ratio during preparation on the catalytic performance of Ni₂P@C for the hydrodechlorination of HCFC-22 at 450 °C, atmospheric pressure and GHSV (gas hourly space velocity) of 480 h⁻¹. (a) Conversion of HCFC-22 as a function of TOS. (b) Selectivity to CH_2F_2 (HFC-32) as a function of TOS. (c) Selectivity to CHF_3 (HFC-23) as a function of TOS.



Figure S16 Effect of reaction temperature on the catalytic performance of Ni₂P@C for the hydrodechlorination of HCFC-22 at 450 °C, atmospheric pressure and GHSV of 480 h⁻¹. (a) Conversion of HCFC-22 as a function of TOS. (b) Selectivity to CH_2F_2 (HFC-32) as a function of TOS. (c) Selectivity to CHF_3 (HFC-23) as a function of TOS.



Figure 17 XRD patterns of MoP, CoP and Co_2P catalysts prepared by microwave assisted combustion of phytic acid and cobalt nitrate or ammonium molybdate and reduced at 650 °C for 3 h in H₂ atmosphere.



Figure S18 Catalytic performance of Mo_2P , CoP and Co_2P for the hydrodechlorination of HCFC-22 at atmospheric pressure and GHSV of 480 h⁻¹. (a) Conversion of HCFC-22 as a function of TOS. (b) Selectivity to CH_2F_2 (HFC-32) as a function of TOS. (c) Selectivity to CHF_3 (HFC-23) as a function of TOS.