Ni_3P as a High-Performance Catalytic Phase for Hydrodeoxygenation of Phenolic Compounds

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Experimental

Catalyst preparation

Unsupported Ni_3P was synthesised from the oxide precursor by *in situ* H_2 temperature programmed reduction (TPR) method. The oxide precursor was prepared as follows. 13.2 g $Ni(NO_3)_2\cdot6H_2O$ was dissolved in deionized water under stirring to form a clear green solution, and the aqueous solution containing 2.0 g $(NH_4)_2HPO_4$ was then added dropwise under stirring to form a slurry. Afterward, the resultant slurry was heated to evaporate water to obtain a solid product. The product was dried at 120 °C for 12 h and calcined at 500 °C for 3 h. The catalysts were obtained *in situ* by reducing the oxide precursors in hydrogen in the reactor prior to the HDO reaction.

Catalytic HDO

In the aqueous HDO of phenolic compounds catalyzed by Ni_3P, Ni and Pd/SiO_2 (1.0 wt% Pd), Program 2 was used to investigate the dependence of HDO activity on temperature. The HDO reactions were measured under 4.0 MPa H_2, with a flow rate of 100 $mL\cdot min^{-1}$ H_2 and 0.1 $mL\cdot min^{-1}$ liquid feed (flowrate=0.005 $g\text{-phenol}\cdot min^{-1}$). After the reaction system had achieved a steady state (2 h), liquid product was sampled from the gas-liquid separator. The organic products in the sample were extracted by dichloromethane and dehydrated by anhydrous magnesium sulfate. The dried products were analyzed by a gas chromatograph (GC, Agilent 6890, flame ionization detector) with a HP-INNOWax capillary column (30 m × 320 μm × 0.5 μm). The GC detecting conditions were as follows: N_2 as the carrier gas; injection port temperature = 280 °C; detector temperature = 280 °C; initial column temperature = 120 °C, heating up to 230 °C with a heating rate of 10 $°C\cdot min^{-1}$, and stayed at 230 °C for 3 min.

To compare the catalytic performance of unsupported Ni_3P between aqueous and oil phase HDO of phenol, the content of phenol in water was reduced from 5.0 to 1.0 wt%, while the other conditions were not changed.

The thermodynamic equilibrium conversion from phenol to cyclohexanol was calculated by the minimization of the Gibbs free energy, which was made in Aspen Plus 2006 V8.4. The simulation conditions were consistent with the catalytic aqueous phase HDO conditions.

Results and Discussion

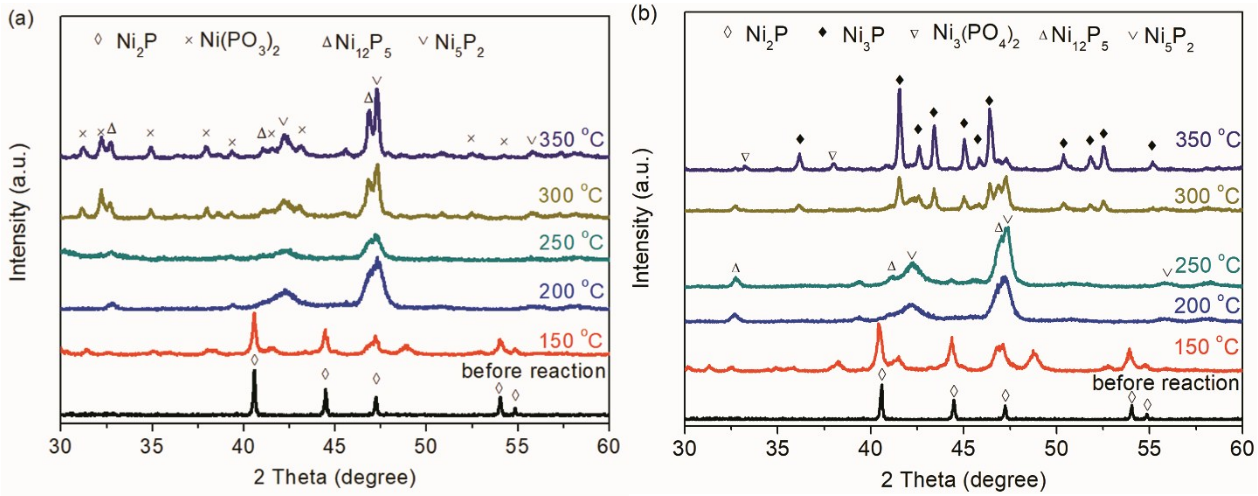

Fig. S1 XRD patterns of the spent catalysts after treatment in water for 2.5 h at various temperatures in comparison with those of fresh Ni_2P using (a) Program 1 and (b) Program 2.

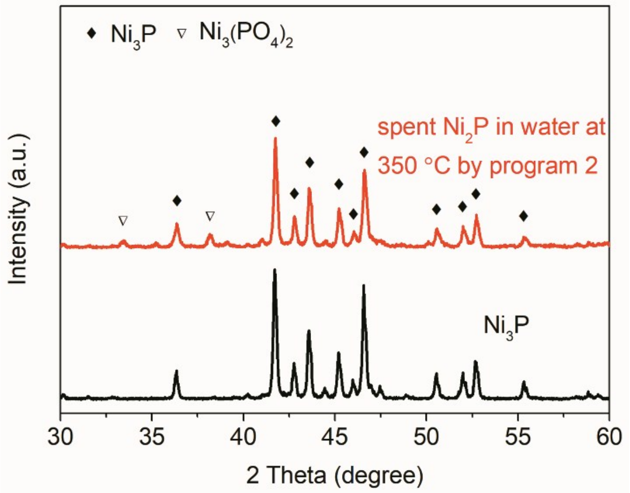

Fig. S2 XRD pattern of the synthesize unsupported Ni_3P in comparison with the spent catalyst after treatment in water at 350 °C by Program 2.

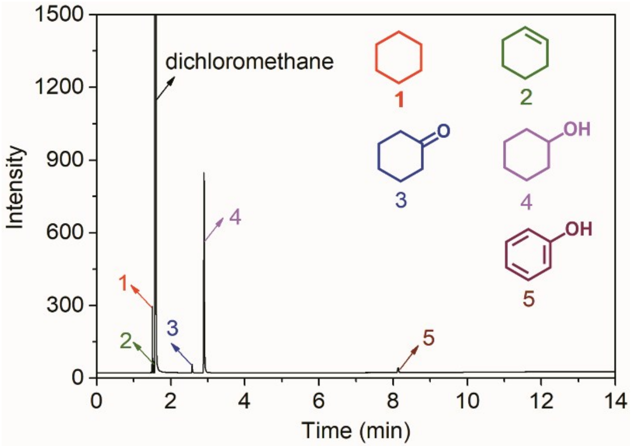

Fig. S3 Representative gas chromatogram of the liquid product from aqueous phase HDO of phenol.

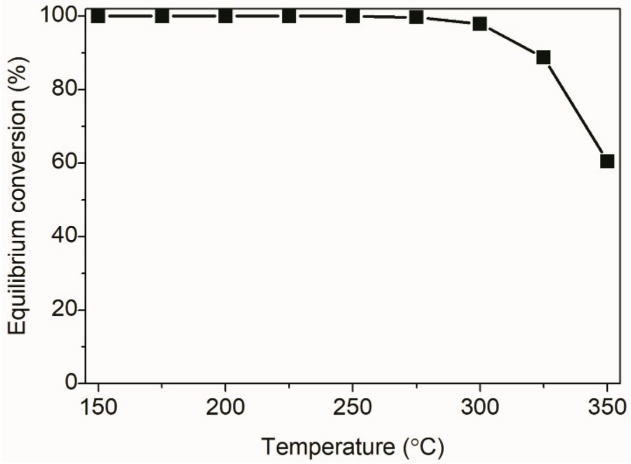

Fig. S4 The equilibrium conversion of phenol hydrogenation to cyclohexanol as a function of temperature.

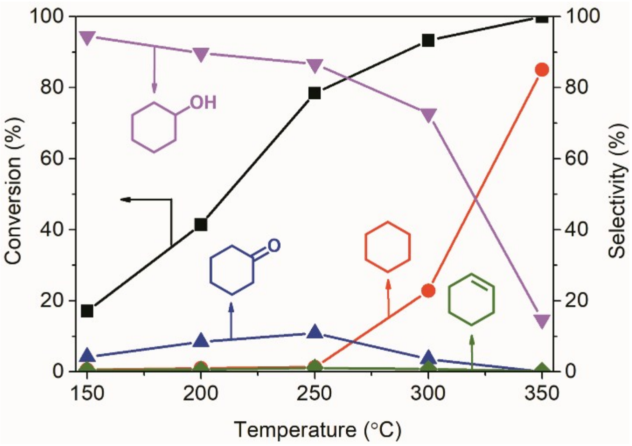

Fig. S5 Catalytic performance of unsupported Ni in aqueous phase HDO of phenol.

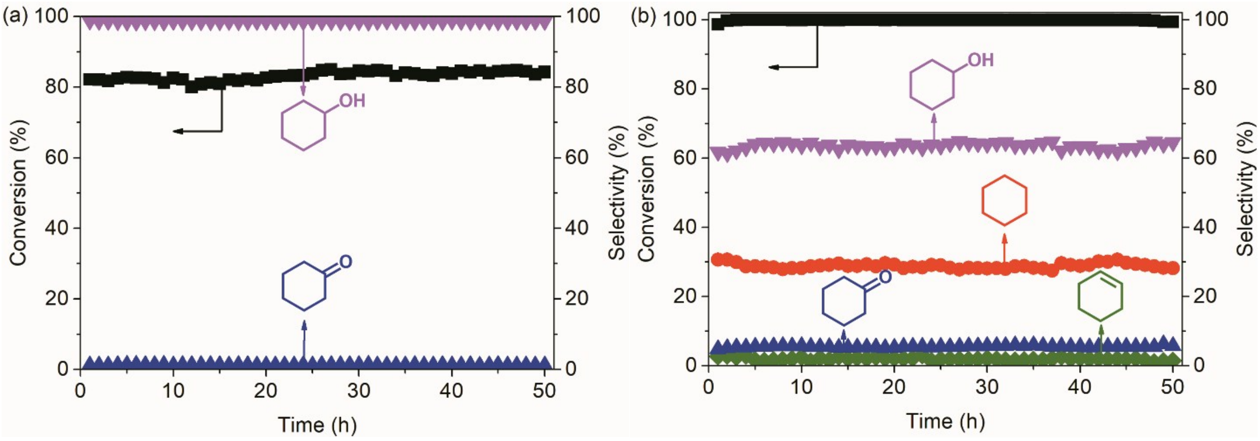

Fig. S6 Variation of phenol conversion and product selectivities with time on stream in aqueous phase HDO over unsupported Ni_3P at 150 °C (a) and 300 °C (b).

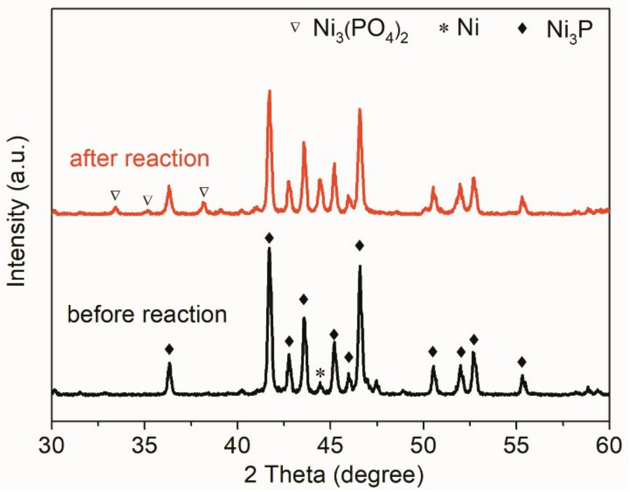

Fig. S7 XRD patterns of unsupported Ni_3P before and after the 50-h run.

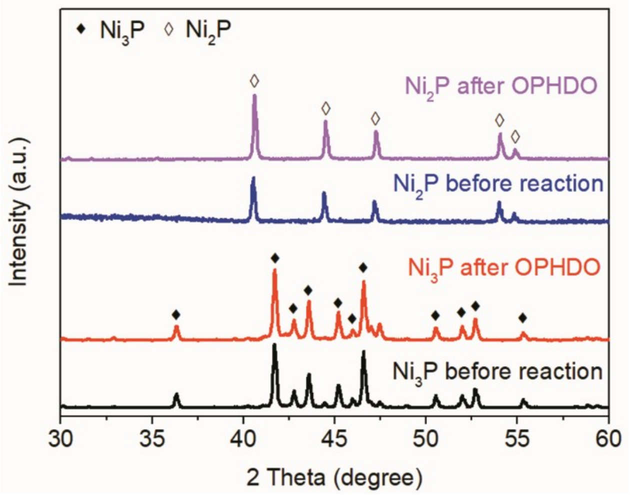

Fig. S8 XRD patterns of the catalysts (unsupported Ni_3P and Ni_2P) before and after oil phase HDO of phenol.

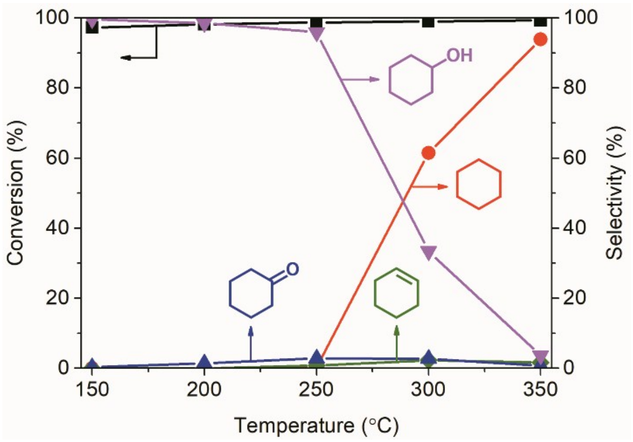

Fig. S9 Catalytic performance of unsupported Ni_3P in aqueous phase HDO of phenol (1.0 wt%).

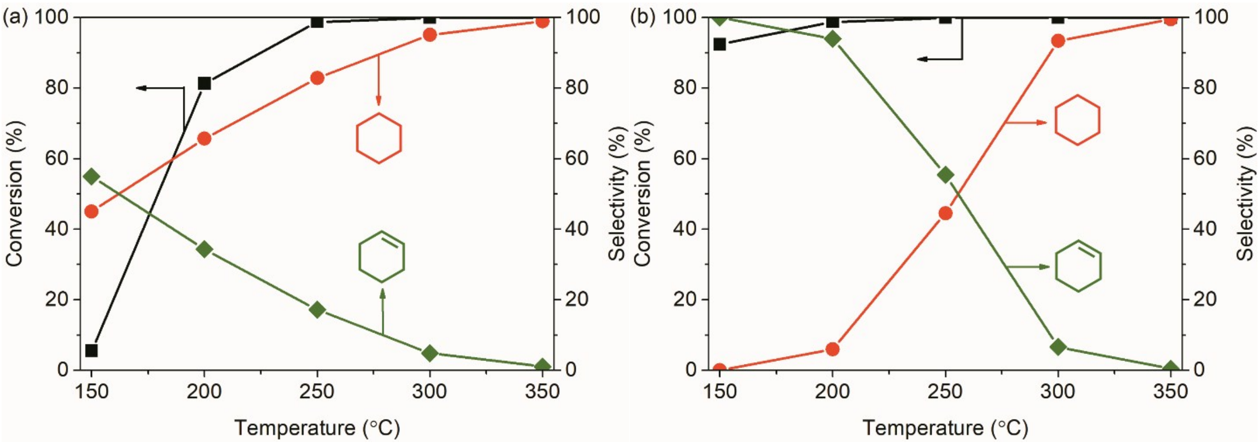

Fig. S10 Variation of cyclohexanol conversion and product selectivities with temperature in oil phase HDO over unsupported (a) Ni_3P and (b) Ni_2P.