

Catalytic system based on nickel(II) acetate and hypophosphorous acid for the selective hydrodeoxygenation of guaiacol

Maria A. Golubeva and Anton L. Maximov

Synthesis of nickel phosphide catalysts and catalytic activity tests

Nickel phosphide catalysts were prepared *in situ* in a stainless-steel autoclave during the process of HDO of guaiacol. The mixture of nickel(II) acetate tetrahydrate (Sigma-Aldrich, 98%), hypophosphorous acid solution (Sigma-Aldrich, 50 wt. % in H₂O) with P : Ni molar ratio = 2 : 1 and 5 wt. % solution of guaiacol (Acros Organics, 99+%) in decaline (Honeywell, mixture of *cis* + *trans*, ≥98%) was dispersed using an ultrasonic disperser to form an inverse emulsion. Then the mixture was put in the autoclave. The initial pressure of H₂ (Air Liquide, ≥98%) was various (3-8 MPa). The autoclave was heated up to 553-653 K. When the temperature became constant, the magnetic stirrer was turned on and the mixture was stirred and heated during 2-8 hours. After the reaction the autoclave was cooled at the room temperature and the gas pressure was released into potassium manganite(VII) (Component-reaktiv, pur.) solution. Liquid products were isolated from the autoclave and were separated from catalyst using centrifuge (5000 rpm). The catalyst was cleaned by acetone, and then residues of acetone were removed by Ar (Air Liquide, ≥98%). The catalyst was dried at 403 K in the oven, and then it was cooled to the room temperature and was cleaned by water to dissolve water-soluble by-products and also was dried at 403 K in the oven.

All experiments with nickel (II) acetate tetrahydrate and hypophosphorous acid separately, as well as recycling tests of catalyst were carried out similarly.

Characterization

Liquid products were analyzed by *Gas Chromatography with Flame-Ionization Detection (GC-FID)* and *Gas Chromatography – Mass Spectrometry (GC-MS)*. Quantitative analysis of liquid products was carried out using a gas-liquid chromatograph Crystallux 4000M with a flame ionization detector, a capillary column SPB-1 (Supelco, 30 m x 0.25 mm x 0.25 μ m), helium as a carrier gas. Qualitative analysis of liquid products was carried out using a gas-liquid chromatograph Finnigan MAT 95 XL with a mass-spectrometry detector, a capillary column Varian VF-5MS (30 m x 0.25 mm x 0.25 μ m) and also helium as a carrier gas.

The composition of catalysts was characterized by *X-Ray diffraction (XRD)* analysis, which was carried out using a Rigaku Rotaflex RU-200 diffractometer (CuK α radiation) in the range of 5-100° 2 θ , with a goniometer (Rigaku D/Max-RC), a rotation speed of 1° 2 θ /min, a step 0.04°.

X-ray fluorescence analysis (XRF) was carried out using an X-ray fluorescence wave spectrometer ARL Perform'X (Thermo Fisher Scientific, New Wave).

Transmission electron microscopy (TEM) and elemental mapping measurements were studied using LEO912 AB OMEGA, zoom from 80 \times to 500000 \times , image resolution: 0.2 – 0.34 nm.

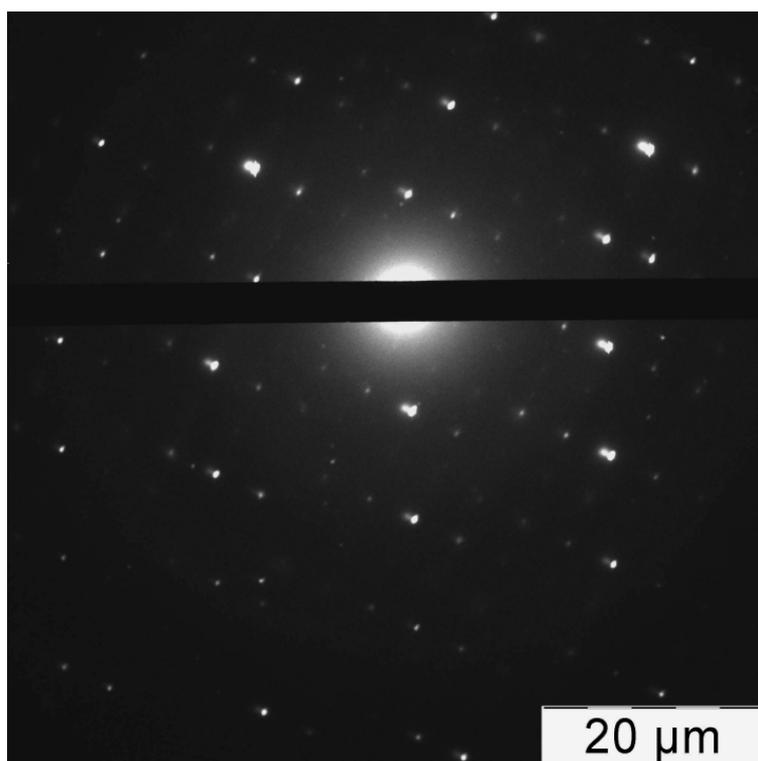


Figure S1 Electron diffraction pattern of nickel phosphide catalyst

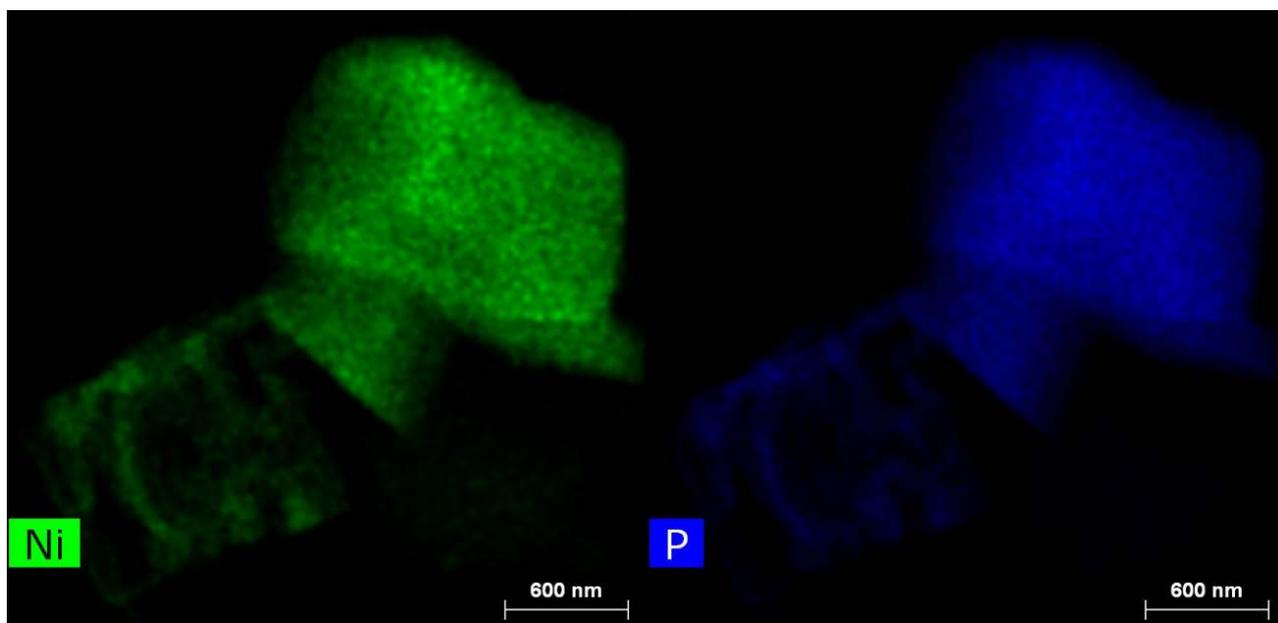


Figure S2 Elemental (nickel, phosphorus) mapping analysis of catalyst

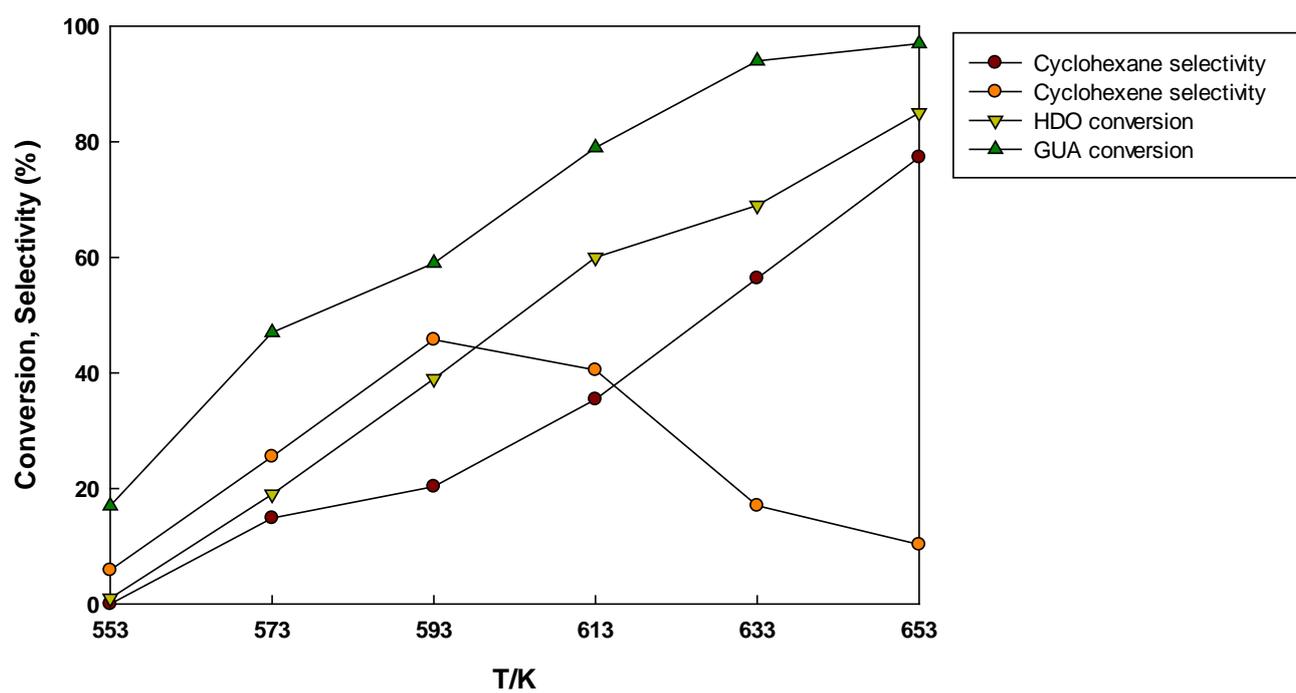


Figure S3 Results of guaiacol HYD over catalytic system based on nickel(II) acetate and hypophosphorous acid. Conditions: 5 wt. % of guaiacol in decaline, molar ratio P/Ni = 2 : 1, substrate/Ni = 25 : 1, T = 553-653 K, $p(\text{H}_2)$ = 6 MPa, t = 6 h

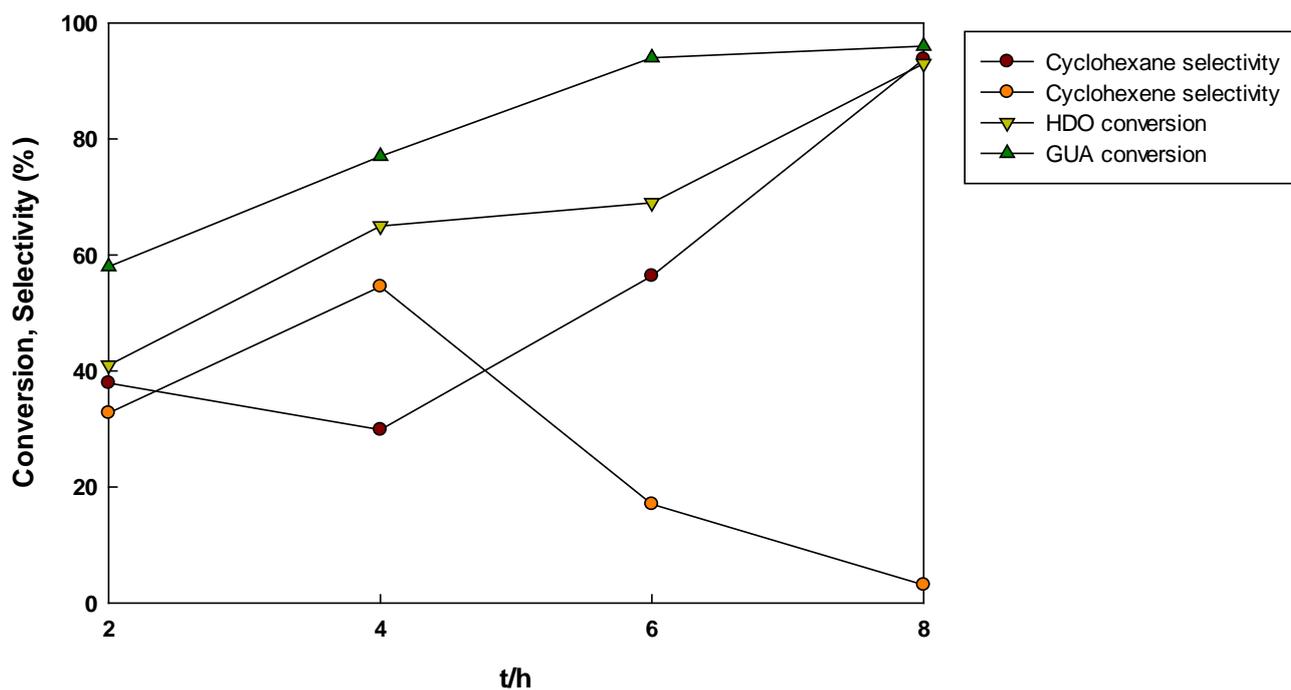


Figure S4 Results of guaiacol HYD over catalytic system based on nickel(II) acetate and hypophosphorous acid. Conditions: 5 wt. % of guaiacol in decaline, molar ratio P/Ni = 2 : 1, substrate/Ni = 25 : 1, T = 633 K, p(H₂) = 6 MPa, t = 2-8 h

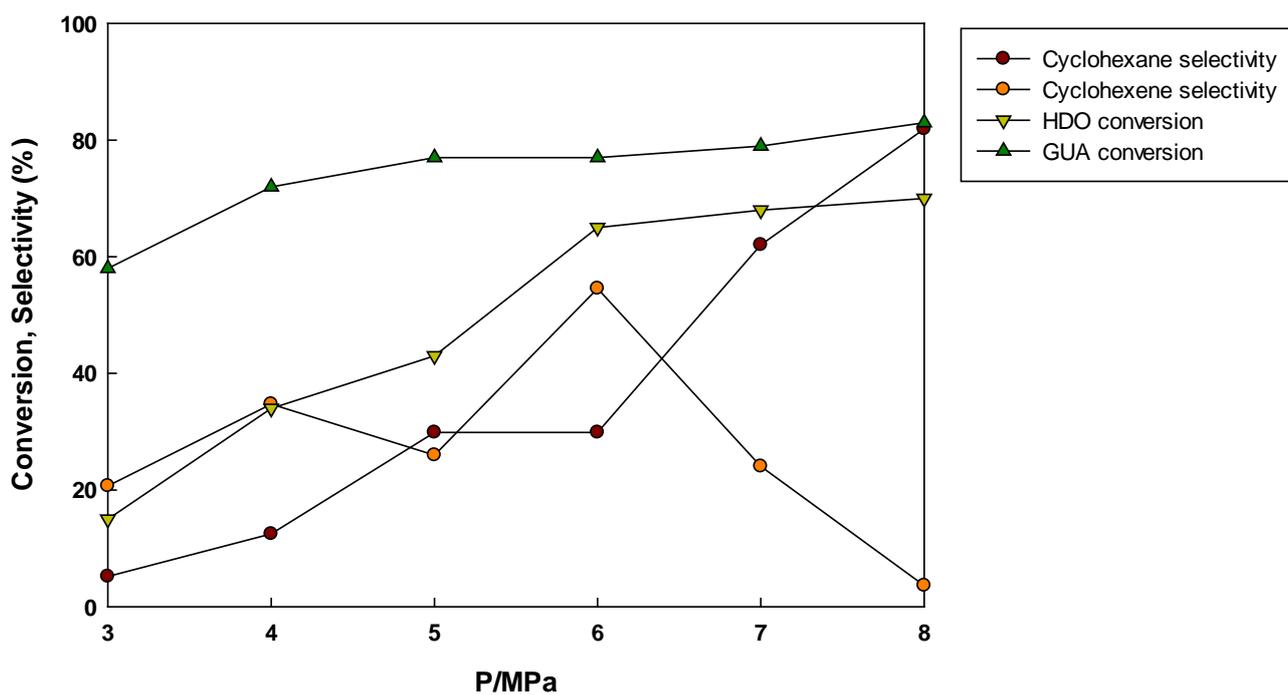


Figure S5 Results of guaiacol HYD over catalytic system based on nickel(II) acetate and hypophosphorous acid. Conditions: 5 wt. % of guaiacol in 2 ml of decaline, molar ratio P/Ni = 2 : 1, substrate/Ni = 25 : 1, T = 633 K, p(H₂) = 3-8 MPa, t = 4 h

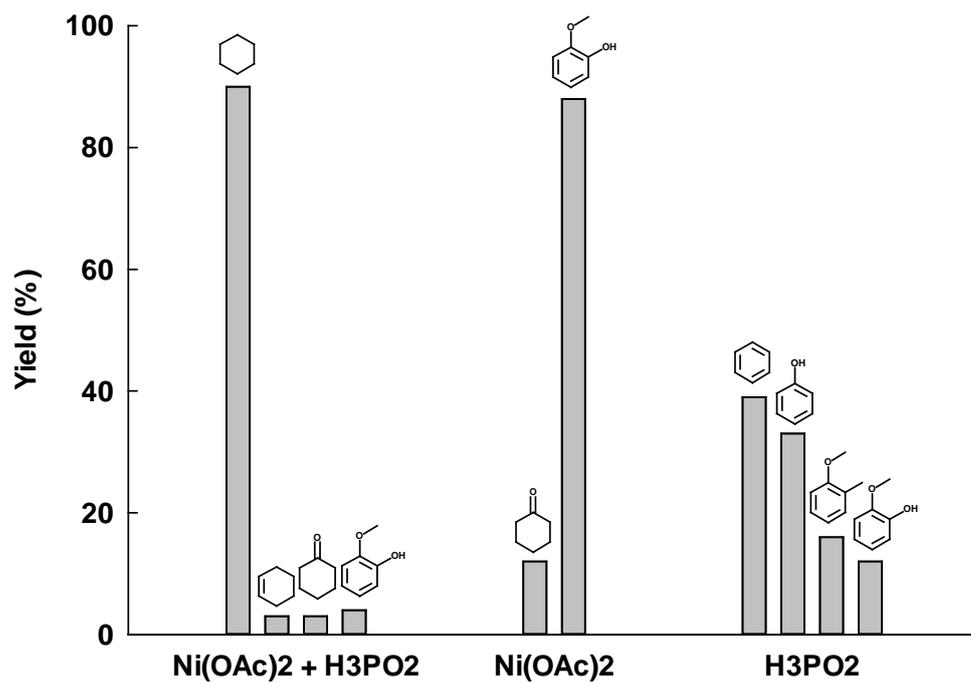


Figure S6 Hydroconversion products of guaiacol over different types of catalytic system (633 K, 6 MPa, 8 h, substrate : Ni = 25 : 1, substrate: P = 12.5 : 1)

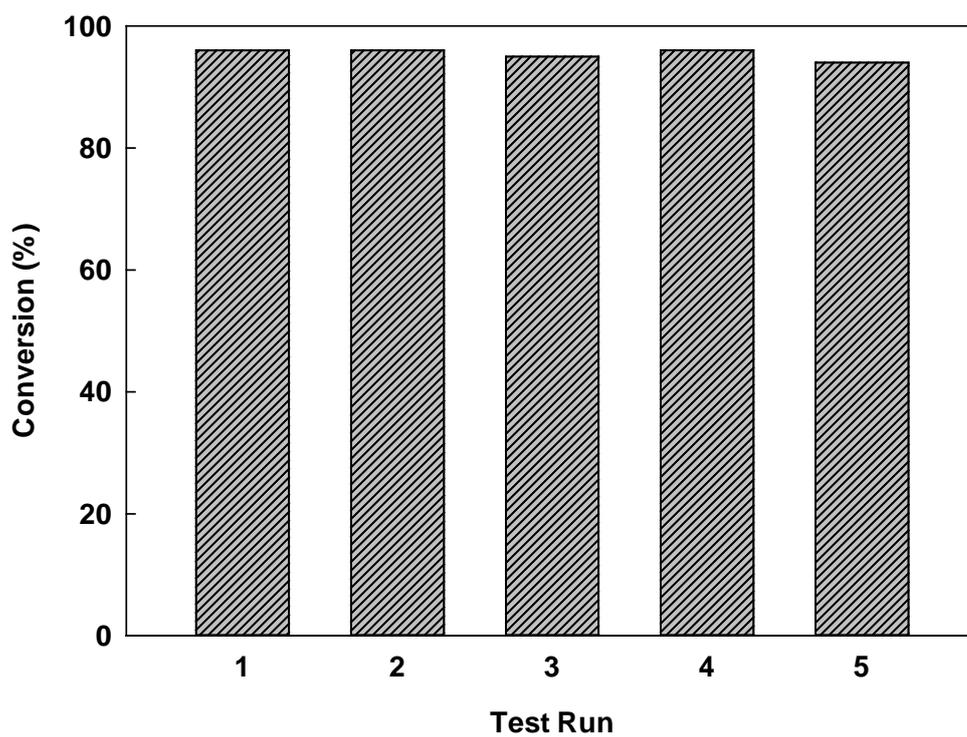


Figure S7 The five run recycling test of nickel phosphide catalyst (633 K, 6 MPa H₂, 8h)

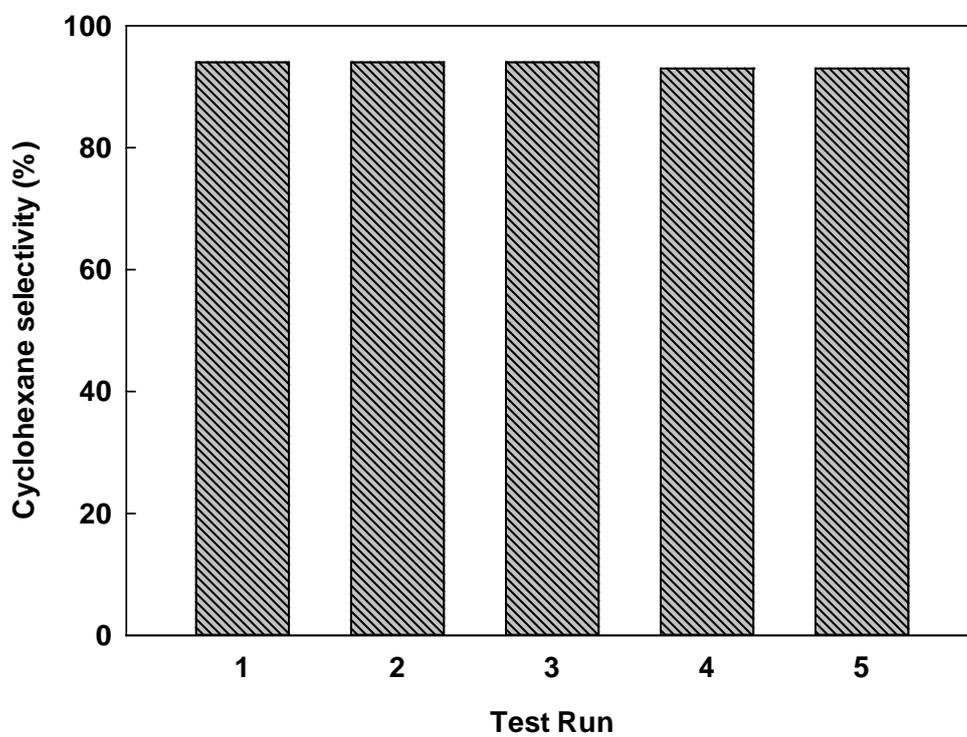


Figure S8 The five run recycling test of nickel phosphide catalyst (633 K, 6 MPa H₂, 8h)