

Enhanced Selective Production of Arenes and Regenerating Rate in Aryl Ether Hydrogenolysis over Mesoporous Nickel in Plug-Flow Reactors

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1. Materials

Ordered KIT-6 mesoporous silica was purchased from XFNano Co. Ltd, China. The following chemicals were purchased from the Sinopharm Chemical Reagent Co. Ltd and used as received: nickel(II) nitrate nonahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethyldisilazane (HMDS, 98.5%), hydrazine hydrate (85%), sodium hydroxide (99%), toluene (anhydrous, 99% purity), aqueous ammonia (25 wt.%), n-hexane (97%), sodium hydroxide (99%), 2-propanol (HPLC grade, 99.7%), ethanol (99.8%), sucrose(99%), urea (99%), dodecane (anhydrous, 99%), anisole (99%), catechol (99%), guaiacol (98%) and Raney Ni (99.9%). cyclohexanol (99%), phenol (99%), were purchased from Aladdin Co. Ltd, China and used without further purification. Benzyl phenyl ether (BPE) was purchased from Tokyo Chemical Industry Co. Ltd, Shanghai, China (TCI). Purified water (EASYPure II, resistivity: $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$) were also received and used without further purification.

2. Catalysts characterizations

In order to characterize the structures of these materials, scanning electron microscopy (SEM) was recorded on a JSM-7000 at 20 kV. The power samples were used without any pretreatment. Transmission electron micrographs (TEM) were recorded on a JEM 2100, 200

kV transmission microscope operated at 120 kV. Prior to the recording, samples were prepared by suspension in ethanol, assisted by sonication and followed by deposition on a copper grid-supported carbon film. The average cluster size was obtained by counting 80 metal particles. Low and high angle X-ray powder diffraction (XRD) was performed on a Bruker D8 diffractometer with Cu K α radiation with a λ of 1.54 Å. The average particle size of Ni in the catalyst can be calculated by the Debye-Scherrer equation. N₂ adsorption-desorption was carried out by using a Micromeritics ASAP 2020 automated system. The Brunauer-Emmett-Teller (BET) method determines the surface area of the catalyst, and the Barrett-Joyner-Halanda (BJH) method determines the pore volume and average pore size.

3. Kinetic study in a batch reactor

The hydrogenolysis reaction was carried out in a stirred autoclave (Anhui Kemi Mechanical Instrument, 4560 Small Reactor System), and the stirred high pressure reactor have a PTFE insert. In the experiment, the reactor was charged with 20.0 mg of catalyst (exposure to air) and 80 mL of lignin model compound (5.0-10.0 mmol L⁻¹ in 2-PrOH). Further, dodecane was added to the reaction vessel as an internal standard (40 g L⁻¹, 60 μ L). The reactor was washed three times with N₂ (99.99%) and then pressurized to the desired pressure at the reactor port. After the pressure was stabilized, the reactor was heated to the temperature required at a stirring speed of 650 rpm. The temperature is kept at 4 to 8 hours, and the length of time is determined by the activity of the catalyst. After a constant temperature of 30 minutes (induction period), the hot reaction mixture was sampled at regular intervals. The reactor was finally cooled to room temperature by means of an ice water bath. The liquid product was collected at room temperature and pressure and the liquid product was placed in a gas-liquid separator for quantitative analysis. The reaction products were analyzed and quantified by gas chromatograph-mass spectrometry (GC-MS, Shimadzu QP-2010 Ultra, equipped with an Agilent HP-5MS capillary column, 30 m \times 0.25 μ m \times 0.25 μ m, injection volume 1 μ L). The catalyst was collected with a magnet, tested for stability, and thoroughly washed with 2-PrOH. The catalyst used again was used under the same reaction conditions. Each catalyst was repeated three times. Curve fitting was performed using the concentration average of each time interval.

4. Analysis of reaction products

The reaction product was quantified using gas chromatography-flame ionization detection (GC-FID, Shimadzu GC-2010, equipped with an Agilent HP-5 capillary column, 30 m × 0.25 μm × 0.25 μm, injection volume 1 μL). The response factor of the compound can be obtained from the constructed calibration curve. Calculation of conversion and selectivity was performed based on the number of moles of carbon. The sum of the hydrogenolysis product yields should be 100 mol%. In all experiments, the carbon balance was better than (95 ± 3)%.

5. Analysis of adsorbed species

After the activity of the Ni-based catalyst is tested, the temperature of the reactor is lowered to room temperature. The catalyst bed was rinsed overnight with a low flow rate (0.1 mL min⁻¹) with 2-PrOH (n-dodecane as internal standard) which allowed removal of the BPE physically adsorbed on the catalyst. Then, the temperature was raised to 205 °C at a rate of 5 degrees per minute. Some samples were collected from the reactor every 5 minutes and analyzed by gas chromatography-mass spectrometry (injection amount 5 μL). Blank experiments were performed without catalyst prior to analysis.

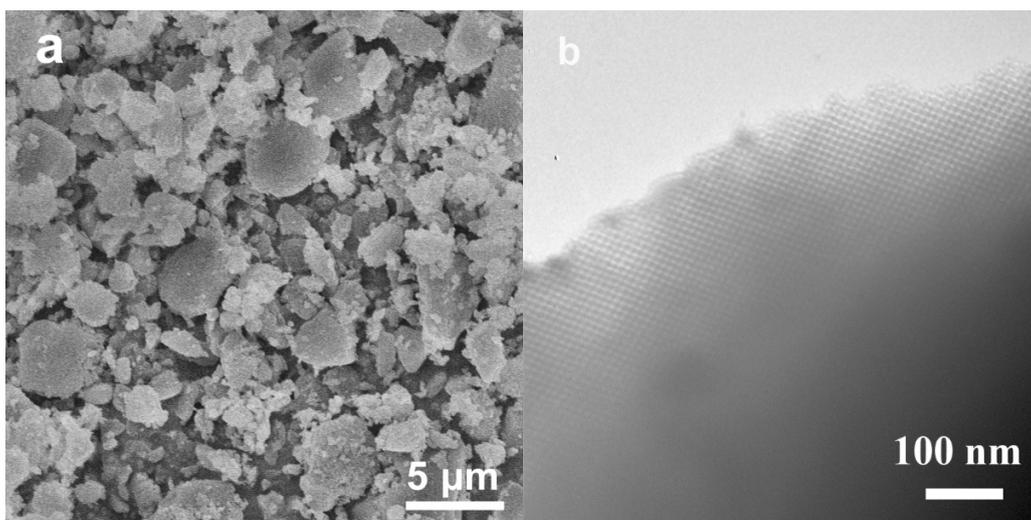


Figure S1. (a) Scanning electron microscope (SEM) image and (b) transmission electron microscope (TEM) image of mesoporous silica KIT-6.

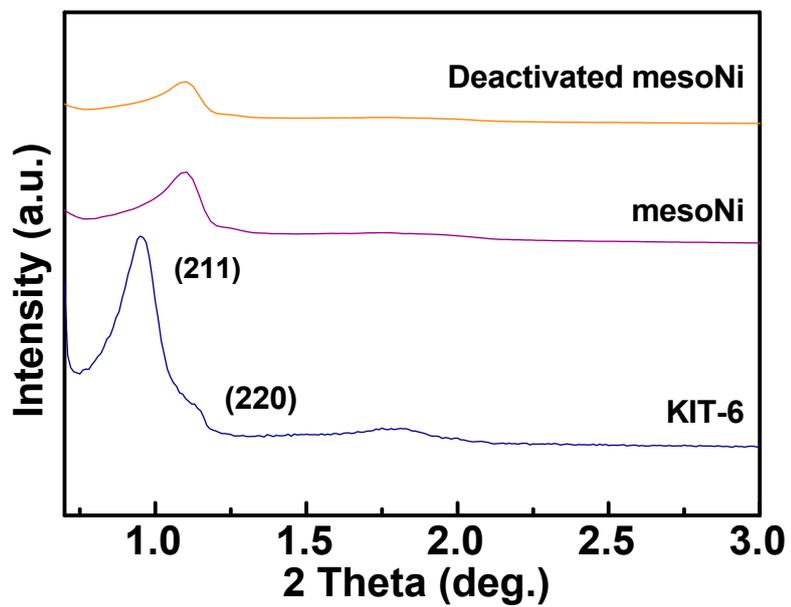


Figure S2. Small-angle XRD patterns of ordered mesoporous Ni made using KIT-6 as a hard template, before and after use in benzyl phenyl ether (BPE) hydrogenolysis.

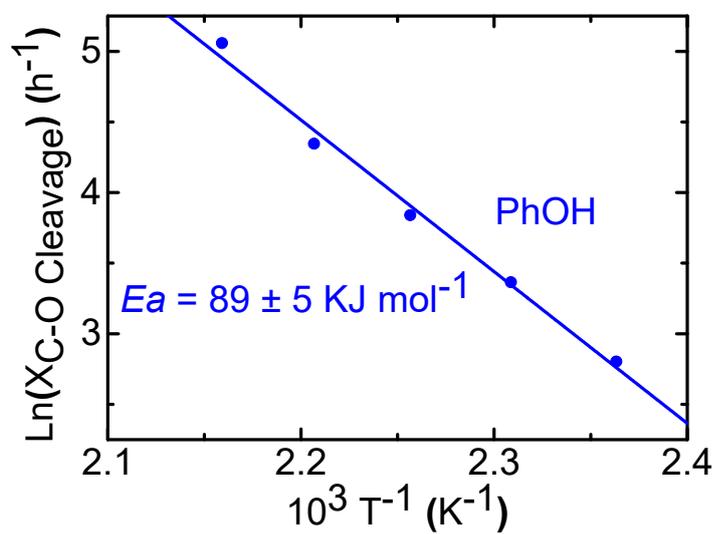


Figure S3. Arrhenius plot and apparent activation energy ($E_{a,app}$) for hydrogenolysis of phenol. Reaction conditions: 20.0 mg catalyst, 2-propanol as both solvent and H-donor, pressure 4 MPa, 5.0 mmol·L⁻¹ BPE, TOS = 60 min.

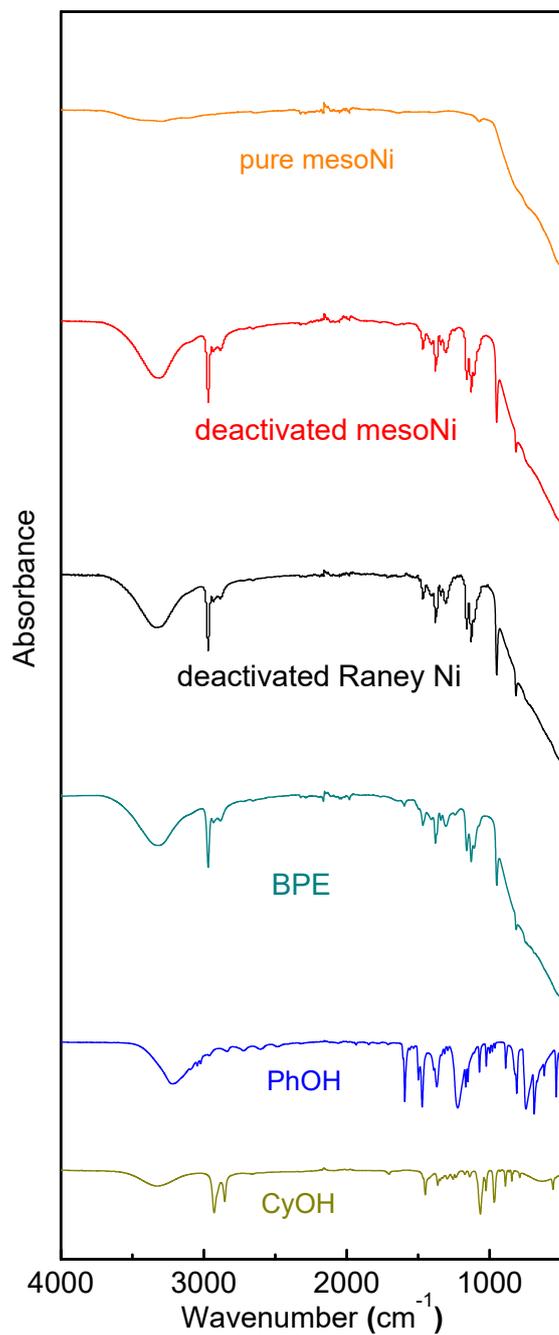


Figure S4. ATR-IR spectra of used Ni-based catalysts compared to cyclohexanol, phenol and benzyl phenyl ether (BPE). Reaction conditions: 120 °C, 20.0 mg catalyst, 80 mL 2-PrOH as both solvent and H-donor, pressure 4 MPa, 5.0 mmol·L⁻¹ BPE, stirring at 650 rpm.

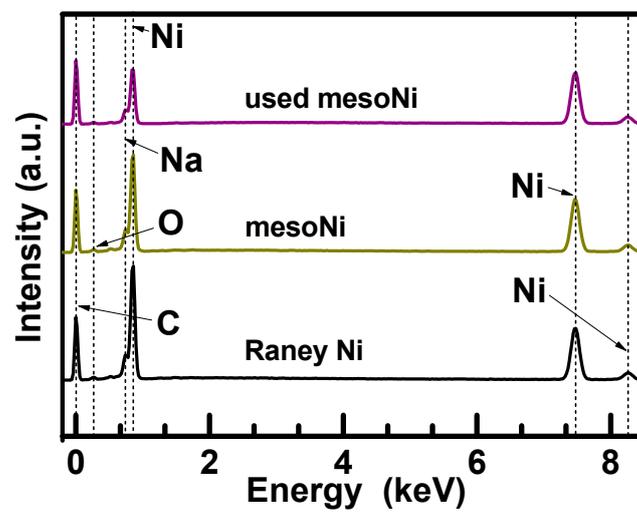
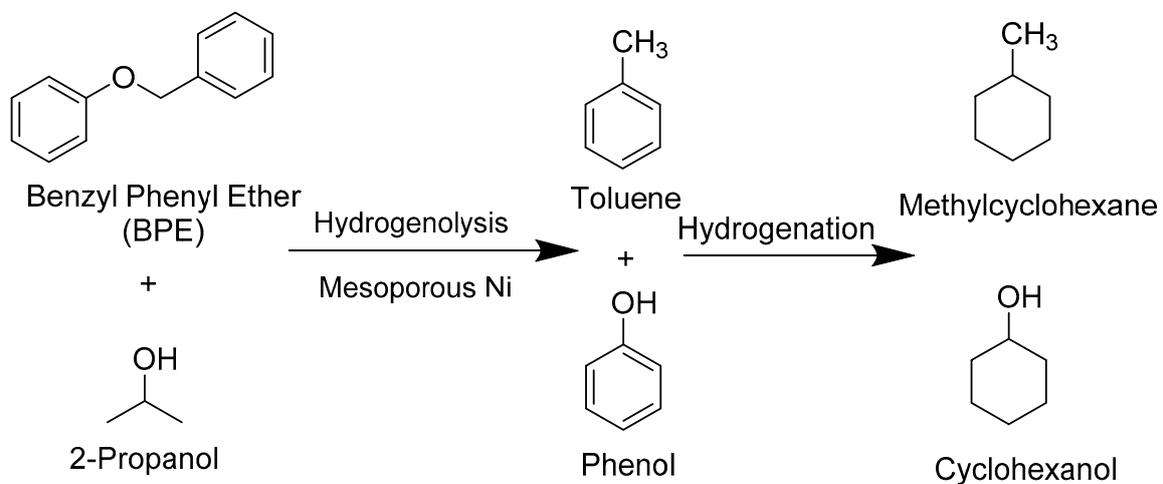


Figure S5 EDX characterization of Raney Ni, fresh and used mesoporous nickel catalyst (mesoNi).



Scheme S1 Major products over Ni-based catalysts, indicating two sequential reaction pathways: C–O bond hydrogenolysis to toluene and phenol, and subsequent hydrogenation of phenyl ring to methylcyclohexane and cyclohexanol.