

Selective production of bio-based *para*-xylene over FeOx-modified Pd/Al₂O₃ catalyst

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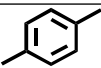


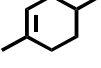
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1.

| Structure | Nomenclature | Abbreviation |
|---|--------------------------|--------------|
|  | Para-xylene | PX |
|  | Methyl cyclohexane | MCA |
|  | 4-Methyl-cyclohexene | MCE |
|  | 1,4-Dimethyl-cyclohexene | DMCE |

2. Catalyst preparation

All the catalysts were prepared by incipient wetness impregnation method. For 1Pd_nFeOx/Al₂O₃ (n=1, 3, 5, 7, 10, 15) catalysts, the support Al₂O₃ was impregnated in PdCl₂ aqueous solution for 5 h, followed by drying at 80 °C for 12 h. Then the obtained sample was impregnated in Fe(NO₃)₃ aqueous solution with calculated concentration. At last, the 1Pd_nFeOx/Al₂O₃ catalyst was obtained by drying at 80 °C for 12 h and calcination at 500 °C for 4 h. 1Pd/Al₂O₃ or 10FeOx/Al₂O₃ catalyst was prepared with the similar procedure only without impregnation of PdCl₂ or Fe(NO₃)₃ aqueous solution. The nominal Pd loading of all the Pd-based catalysts is 1 wt%, and n indicates n% weight loading of Fe in 1Pd_nFeOx/Al₂O₃ catalyst.

3. Catalyst characterization

N₂ adsorption-desorption isotherms were performed at -196 °C with an ASAP-2010. Before N₂ adsorption, the samples were pretreated in a vacuum at 100 °C for 1 h and 300 °C for 4 h and then switched to the analysis station for adsorption-desorption analysis.

X-ray powder diffraction (XRD) was recorded in the 2θ range of 10–90° (scan rate = 5°/min) on an X'pert Pro PAN analytical X-ray diffractometer with a Ni-filtered Cu Ka radiation (40 kV, 30 mA). Prior to XRD experiments, the catalysts were reduced at 350 °C for 2 h.

TEM and HRSTEM of the reduced catalysts at 350 °C for 2 h were performed on a JEM-2100F high-resolution transmission electron microscope equipped with an energy-dispersive X-ray (EDX) detector operating at 200 kV.

H₂-TPR was carried out with a Micromeritics AutoChem 2920 apparatus. Prior to the measurement, the catalyst sample was pretreated in Ar flow at 120 °C for 2 h. After cooling to room temperature in Ar, the gas flow was switched to 10% H₂/Ar and the sample was heated from room temperature to 800 °C with a temperature ramp of 5 °C/min. The results were recorded by Mass spectrum and TCD detector.

The in situ CO-FTIR and Propanal-FTIR was performed on an infrared spectrometer (VEREX70, Bruker, Germany). Prior to the adsorption of CO/propanal, the catalysts were reduced in H₂ flow (20 ml min⁻¹) at 350 °C for 2 h, purged with He for 0.5 h and cooled down to 20 °C. Then the samples were purged with helium and the CO-FTIR spectra were recorded.

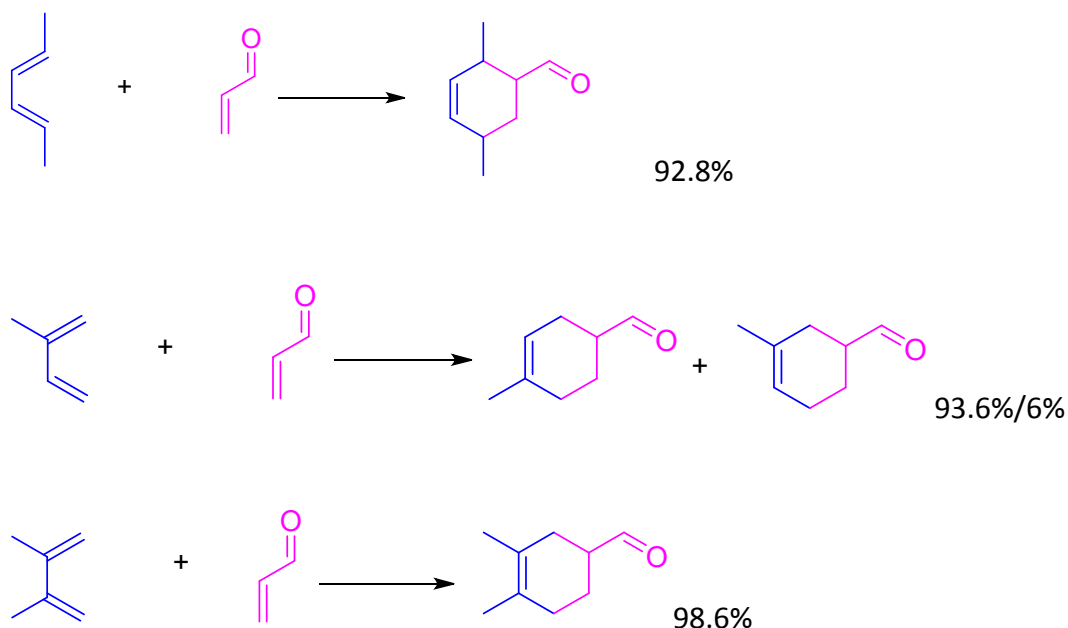
X-ray photoelectron spectroscopy (XPS) patterns of the samples (at 350 °C for 2 h) were conducted on a Kratos AXIS ULTRA DLA X-ray photoelectron spectrometer equipped with a Al Kα radiation source (1486.6 eV, 15 kV) after reduced in situ at 350 °C for 2h. All binding energies were calibrated with the C1s peak at 284.8 eV for the adventitious carb.

CO-Chemisorption was conducted using dynamic pulse technique on Auto Chem. II 2920 equipment (Micromeritics, USA) at 20 °C using a pulse of 5% CO in He. Prior to the measurement, the samples were reduced in situ by flowing H₂ at 350 °C for 2 h and then purged with He for 30 min to remove hydrogen species adsorbed on the surface.

4. General procedure for the Diels–Alder reaction: In a typical reaction, isoprene (30 mmol) was added slowly to ionic liquid $[\text{Bmim}]\text{Zn}_2\text{Cl}_5$ (2.5 mmol) and acrolein (25 mmol) at 25 °C under vigorous stirring for 24 h. Then, two phases were formed and the upper clear liquid was pipetted off for gas chromatographic analysis [Agilent Technologies 6890N, flame ionization detector (FID), 30 m x 0.32 mm x 0.25 mm HP-5 column, N_2 as carrier gas] with external standard. The isolated products were further purified by distillation (125 °C, 2 KPa) to afford the two regioselective cycloadducts para- and meta-MCHCA. The ionic liquid phase (bottom) was washed with hexane, purified under vacuum, and directly reused in subsequent runs.

5. Supplemental results






5.1 Diels-Alder reaction results of acrolein with different dienes



Reaction Conditions: diene (0.30 mol), dienophile (0.24 mol), $[\text{Bmim}]\text{Zn}_2\text{Cl}_5$ (10 mmol), reacting at 25 °C for 24 h.

5.2

Table S1. Catalytic conversion of 4-MCHCA to *p*-xylene over 1Pd10Fe/Al₂O₃ at different temperature.

| Entry | Catalyst | Con. (%) | Temp. (°C) | Yield (%) | | | | |
|-------|--|----------|------------|---|--|---|---|---|
| | | | |  |  |  |  |  |
| 1 | 1Pd10FeOx/Al ₂ O ₃ | 100 | 275 | 17.0 | 8.5 | 15.7 | 44.5 | 5.8 |
| 2 | 1Pd10FeOx/Al ₂ O ₃ | 100 | 300 | 4.1 | 18.9 | 4.0 | 70.1 | 2.8 |
| 3 | 1Pd10FeOx/Al ₂ O ₃ | 100 | 325 | 0.9 | 16.1 | 1.0 | 81.1 | 0.9 |
| 4 | 1Pd10FeOx/Al ₂ O ₃ | 100 | 375 | 0.2 | 16.0 | 1.1 | 80.0 | 2.7 |

Reaction conditions: 4-MCHCA concentration: 20 mg/mL; solvent: hexane; Flow rate of feed solution: 2.5 mL/min; Catalyst: 0.25 g; Carrier gas: H₂ (10 ml·min⁻¹).

5.3

Table S2. CO-Chemisorption results of the catalysts.

| Catalyst | Metal content (wt. %) | | CO chemisorption (μmol/g ⁻¹) |
|--|-----------------------|----|--|
| | Pd | Fe | |
| 1Pd/Al ₂ O ₃ | 1 | 0 | 17.49 |
| 1Pd1FeOx/Al ₂ O ₃ | 1 | 1 | 18.89 |
| 1Pd5FeOx/Al ₂ O ₃ | 1 | 5 | 4.89 |
| 1Pd10FeOx/Al ₂ O ₃ | 1 | 10 | 4.64 |
| 10FeOx/Al ₂ O ₃ | 0 | 10 | 0 |

5.4

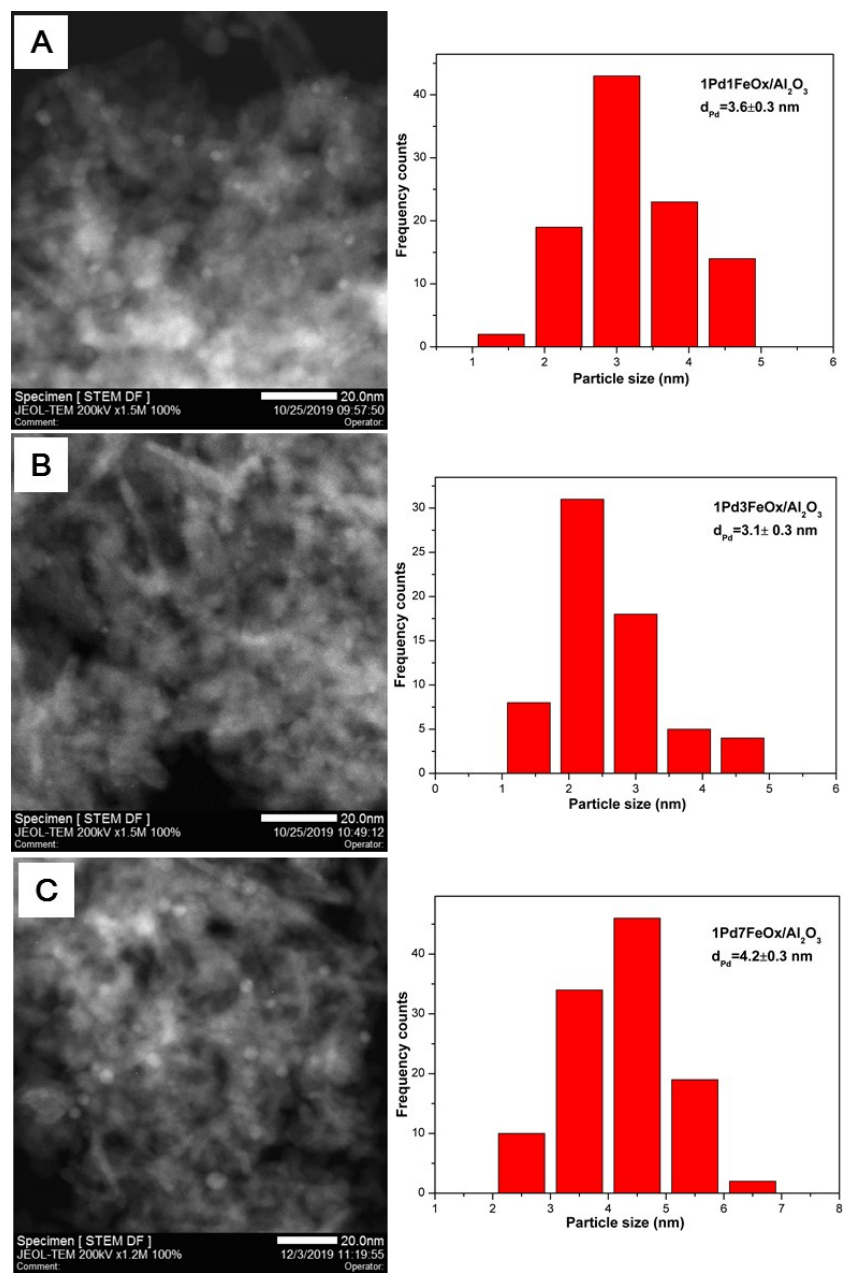


Figure S1. Representative STEM images of (A) 1Pd1FeOx/Al₂O₃; (B) 1Pd3FeOx/Al₂O₃; (C) 1Pd7FeOx/Al₂O₃ and distribution of Pd nanoparticle sizes determined by STEM.

5.5

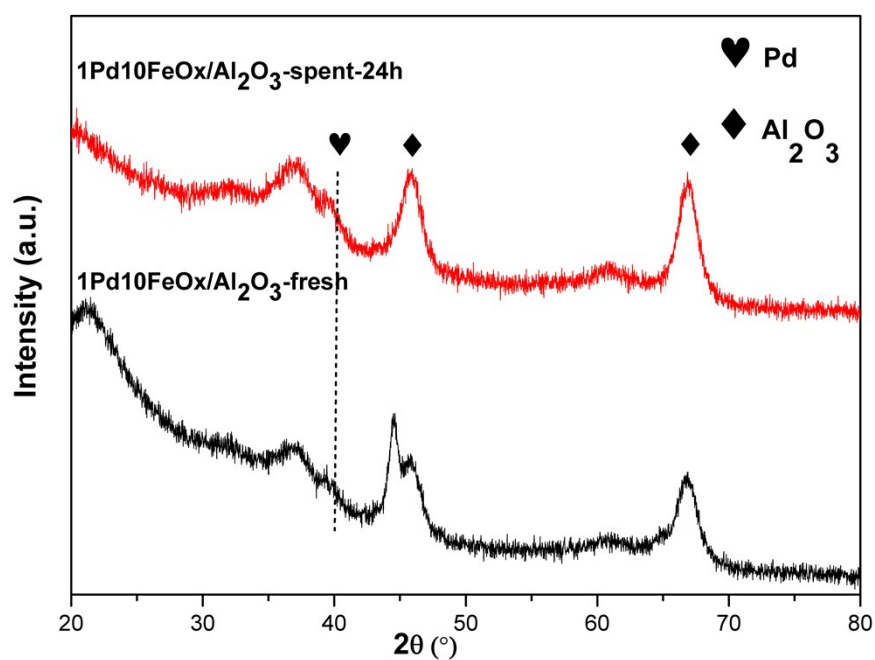


Figure S2. XRD patterns of freshly reduced and used 1Pd10FeO_x/Al₂O₃ catalysts.

5.6

Table S3. BET results of the catalysts.

| Entry | Catalyst | Surface Area (cm ² /g) | Pore volume (cm ³ /g) | Pore diameter (nm) |
|-------|---|--------------------------------------|--|--------------------------|
| 1 | Al ₂ O ₃ | 207.223 | 0.775 | 12.471 |
| 2 | 1Pd/Al ₂ O ₃ | 206.042 | 0.753 | 12.435 |
| 3 | 1Pd1FeO _x /Al ₂ O ₃ | 198.75 | 0.724 | 12.405 |
| 4 | 1Pd3FeO _x /Al ₂ O ₃ | 197.322 | 0.704 | 12.320 |
| 5 | 1Pd5FeO _x /Al ₂ O ₃ | 190.445 | 0.688 | 12.475 |
| 6 | 1Pd7FeO _x /Al ₂ O ₃ | 189.345 | 0.647 | 12.337 |
| 7 | 1Pd10FeO _x /Al ₂ O ₃ | 177.666 | 0.533 | 9.606 |