Electronic Supplementary Information

Hydrodeoxygenation of anisole to benzene over Fe$_2$P catalyst by a
direct deoxygenation pathway

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**1. Figures**

**Fig. S1** Route for the synthesis of Fe$_2$P catalyst by a two-step phosphorization method. The first step is the reduction of Fe$_2$O$_3$ to α-Fe. The second step is heating the NaH$_2$PO$_2$ to produce PH$_3$ to phosphatize the α-Fe.
Fig. S2 SEM images and XRD patterns of Fe₂P prepared via TPR method.
**Fig. S3** MS signal of PH$_3$ (m/e = 34) during the reduction of Fe$_2$P catalyst.
Fig. S4 Selectivity of benzene, 2-methylanisole, phenol and cyclohexane as a function of anisole conversion measured via different space of anisole (200 °C, 0.1 MPa, H₂/anisole = 50).
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Fig. S6 The arene selectivity of different catalysts upon different evaluation conditions (temperature and pressure). The references are followed:

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Fig. S16 Top (a) and side (b) view of Fe$_2$P(101) surface.
Fig. S17 Adsorption configurations and adsorption energies of H atoms on Fe$_2$P(101) surface. Bri-bri (a), bri-hole (b) and hole-hole (c) configurations. (C: gray, O: red, H: white).
Fig. S18 Energy profiles of H₂ dissociation on the Fe₂P(101) surface and the correspond barrier is given in the parenthesis.
### 2. Tables

**Table S1** XPS spectra of Fe2p of Fe$_2$P catalyst.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>fresh</th>
<th>spent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$^{0}$</td>
<td>Fe$^{2+}$</td>
</tr>
<tr>
<td>Fe$_2$P</td>
<td>46.9</td>
<td>53.1</td>
</tr>
</tbody>
</table>
3. Kinetic measurements

Kinetic measurements of vapor phase anisole hydrodeoxygenation on Fe\textsubscript{2}P catalysts

(1) The absence of heat transfer was checked by Mears’ criterion\textsuperscript{1,2}:

\[ C_M = \left( \frac{-\Delta H_{\text{obs}} p_b R E}{h T^2 R_g} \right) \]

Where \( \Delta H \) = heat of reaction (for \( C_7H_8O + H_2 \rightarrow C_6H_6 + CH_3OH \))

\( r_{\text{obs}} \) = observed reaction rate, kmol/kg\_cat\cdot s

\( p_b \) = density of catalyst bed, kg/m\textsuperscript{3}

\( R \) = catalyst particle radius, m

\( E \) = activation energy, kJ/mol

\( h \) = heat transfer coefficient between gas and pellet, J/m\textsuperscript{2}\cdot s\cdot K

\( R_g \) = gas constant, kJ/mol\cdot K

\( T \) = reaction temperature, K

In the current work, a gas flow rate of 55.3 ml min\textsuperscript{-1} and a catalyst particle size of 0.177-0.250 mm were employed for the kinetic study. And the concentration of anisole employed in the feed was 1.96 % (the molar ratio of H\textsubscript{2} and anisole is 50:1).

First, the Reynolds number (Re) is calculated according to the followed formula:

\[ \text{Re} = \frac{U \rho d_p}{\mu} \]

Where \( U \) = free-stream velocity, m/s

\( \rho \) = fluid density, kg/m\textsuperscript{3}

\( d_p \) = diameter of pellet, m

\( \mu \) = viscosity, kg/m\cdot s

The viscosity is calculated according to the following formula:

\[ \mu = (2.6693 \times 10^{-5}) \left( \frac{\sqrt{M T}}{\sigma^2 \Omega_\mu} \right) \]

Where \( M \) = molecular weight, g/mol

\( T \) = temperature, K

\( \sigma \) = collision diameter, Å

\( \Omega_\mu \) = collision integrals for use with the Lennard-Jones potential
Since \( Re \ll 1 \), heat transfer coefficient was estimated by assuming \( Nu \) (Nusselt number = \( h \times \frac{d_p}{k_t} \)) = 2, then:

\[
Nu = \frac{hd_p}{k_t} \approx 2
\]

Where \( h \) = heat transfer coefficient, \( J/m^2\cdot s \cdot K \) or Watts/m\(^2\)·K

\( d_p \) = diameter of pellet, m

\( k_t \) = thermal conductivity, \( J/K \cdot m \cdot s \)

For \( H_2 \), the \( k_t \) is calculated using the following formula:

\[
k_t = \left( \tilde{C}_p + \frac{4}{5}R_g \right) \times \frac{\mu}{M}
\]

Where \( R_g \) = universal gas constant, cal/mol·K

\( \mu \) = viscosity, kg/m·s

\( \tilde{C}_p \) = heat capacity J/mol·K

For the Fe\(_2\)P catalyst,

\[
T = 473.15 \text{ K}
\]

\( Re = 5.689 \times 10^{-3} \)

\( \mu = 1.205 \times 10^{-5} \text{ kg/m} \cdot \text{s} \)

\( \tilde{C}_p = 7.159 \text{ cal/mol} \cdot \text{K} \)

\( k_t = 0.243 \text{ J/K} \cdot \text{m} \cdot \text{s} \)

\( \Delta H = -74.6 \text{ kJ/mol} \) (for \( C_7H_8O + H_2 \rightarrow C_6H_6 + CH_3OH \))

\( r_{obs} = 5.571 \times 10^{-7} \text{ kmol/kg}_{cat} \cdot \text{s} \)

\( \rho_b = 1050 \text{ kg/m}^3 \)

\( R = 1.0675 \times 10^{-4} \text{ m} \)

\( E = 7.38 \times 10^{4} \text{ kJ/kmol} \)

\( h = 2.424 \times 10^3 \text{ J/m}^2\cdot\text{s} \cdot \text{K} \)

\( R_g = 8.3145 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \)

\[
\left| - \frac{\Delta H r_{obs} \rho_b R E}{hT^2R_g} \right|
\]
\[
(74.6 \text{ kJ/mol}) \times (5.571 \times 10^{-7} \text{ kmol/kg}_{\text{cat}} \cdot \text{s}) \times (1050 \text{ kg/m}^3) \times (1.0675 \times 10^{-4} \text{ m}) \times (7.38 \times 10^4 \text{ kJ/kmol})
\]
\[
= \frac{(2.424 \times 10^3 \text{ J/m}^2 \cdot \text{s} \cdot \text{K}) \times (473.15 \text{ K})^2 \times (8.3145 \times 10^{-3} \text{ kJ/mol} \cdot \text{K})}{(7.62 \times 10^{-8} < 0.15}
\]

Therefore, heat transfer effect during the kinetic experiment could be neglected.

(2) The absence of mass transport resistances was checked by Weisz-Prater Criterion (\(C_{WP}\)) for Internal Diffusion.\(^3\)

\[
C_{WP} = \frac{r_{\text{obs}} \rho \cdot R_p^2}{D_e C_s} < 1
\]

Where \(r_{\text{obs}}\) = observed reaction rate, \(\text{mol/kg}_{\text{cat}} \cdot \text{s}\)

\(\rho_c\) = density of catalyst pellet, \(\text{kg/m}^3\)

\(R_p\) = catalyst particle radius, \(\text{m}\)

\(D_e\) = effective diffusivity, \(\text{m}^2/\text{s}\)

\(C_s\) = gas concentration of A at the external surface of the catalyst, \(\text{mol/m}^3\).

\(C_s\) is gas concentration of A at the external surface of the catalyst in \(\text{mol/m}^3\). \(C_s\) is calculated according to the following formula: \(^c\)

\[
C_s = C_o = \frac{N_{\text{anisole}}}{V} = \frac{P_{\text{anisole}}}{R_g T}
\]

Where \(P_{\text{anisole}}\) is the pressure of anisole, \(\text{atm}\)

\(T\) = reaction temperature, \(\text{K}\)

\(R_g\) = universal gas constant, \(\text{atm} \cdot \text{cm}^3/\text{mol} \cdot \text{K}\)

The average velocity for the anisole molecular is:

\[
\bar{v} = \frac{8k_b T}{\pi m}
\]

Where \(k_b\) = the Boltzmann constant, \(1.38 \times 10^{-5} \text{ J/K}\)

\(m\) = mass of anisole molecular

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The mean free path in the gas phase is:

\[ \lambda = \frac{1}{\sqrt{2\pi\sigma^2N_{\text{anisole}}/V}} = \frac{R_gT}{\sqrt{2\pi\sigma^2p_{\text{anisole}}/V}} \]

Where \( \sigma \) = molecular diameter, \( 4.3 \times 10^{-8} \) cm

The pore diameter is 0.65 nm (from BJH desorption branch), which is much less than the mean free path (\( \lambda \)). Consequently, pore diffusion will be dominated by Knudsen diffusion and

\[ D_e \approx D_{Kn}(\frac{\lambda}{3}) \]

For the Fe\(_2\)P catalyst,

\[ r_{\text{obs}} = 5.571 \times 10^{-4} \text{ mol/kgcat} \cdot \text{s} \]

\( \rho_c = 1500 \text{ kg/m}^3 \)

\( R_p = 1.0675 \times 10^{-4} \text{ m} \)

\( D_e = 1.10 \times 10^{-6} \text{ m}^2/\text{s} \)

\( C_s = 0.5053 \text{ mol/m}^3 \).

\[ C_{WP} = \frac{r_{\text{obs}}\rho_c R_p^2}{D_e C_s} \]

\[ = \frac{(5.571 \times 10^{-4} \text{ mol/kgcat} \cdot \text{s}) \times (1500 \text{ kg/m}^3) \times (1.0675 \times 10^{-4} \text{ m})^2}{(1.10 \times 10^{-6} \text{ J/m}^2 \cdot \text{s} \cdot \text{K}) \times (0.5053 \text{ mol/m}^3)} \]

\[ = 1.6 \times 10^{-2} < 1 \]

Therefore, internal diffusion effect could be neglected during the kinetic experiments.

(3) The absence of mass transport resistances was checked by Mears’ Criterion (MR) for External Diffusion \(^{[1, 4]}\)

\[ MR = \frac{r_{\text{obs}}\rho_c R_p^n}{k_c C_{Ab}^c} < 0.15 \]
Where \( r_{\text{obs}} \) = observed reaction rate, mol/kg\text{cat} \cdot \text{s}

\( \rho_c \) = density of catalyst pellet, kg/m\(^3\)

\( R_p \) = catalyst particle radius, m

\( n \) = reaction order

\( k_c \) = external mass transfer coefficient, m/s

\( C_{\text{Ab}} \) = bulk gas concentration of A, mol/m\(^3\)

For the H\(_2\)-anisole system, the diffusion coefficient of anisole is calculated based on the following formula: \(^2\)

\[
D_{\text{AB}} = 0.001853 \times \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \times \frac{1}{P \sigma_{\text{AB}}^2 \Omega_{\text{AB}}}}
\]

\[
\Omega_{\text{AB}} = \frac{1.06036}{T^* \epsilon^{0.15610}} + \frac{0.193}{\epsilon^{0.47635 \cdot T^*}} + \frac{1.03578}{\epsilon^{1.52996 \cdot T^*}} + \frac{1.76474}{\epsilon^{3.89411 \cdot T^*}}
\]

Where \( D_{\text{AB}} \) = binary diffusion coefficient of A in B, m\(^2\)/s

\( \phi_p \) = pellet porosity

\( \sigma_c \) = contraction factor

\( \tilde{\tau} \) = tortuosity

\( M_A \) = molecular weight of H\(_2\), g/mol

\( M_B \) = molecular weight of anisole, g/mol

\( P \) = reaction pressure, atm

\( \sigma_{\text{AB}} \) = Lennard-Jones parameter, Å

\( \Omega_{\text{AB}} \) = collision Integral

\[ kT \]

\[ T^* = \frac{kT}{\epsilon} \]

Because Re \( \ll \) 1, the Nusselt number \( (Sh = 2 + 0.6Re^{1/2}Sc^{1/3}) \) can be estimated to be 2 (Sc is Schmidt number, \( Sc = \frac{v}{D_{\text{AB}}} \)). Then,

\[
Sh = \frac{k_c \times d_p}{D_{\text{AB}}} \approx 2
\]
Where $k_c$ = external mass transfer coefficient, m/s

d_p = diameter of pellet, m

For the Fe_2P catalyst,

$r_{obs} = 5.571 \times 10^{-4} \text{ mol/kg}_{\text{cat}} \cdot \text{s}$

$\rho_b = 1050 \text{ kg/m}^3$

$R_p = 1.0675 \times 10^{-4} \text{ m}$

$n = 0.5$

$k_c = 0.56 \text{ m/s}$

$C_{AB} = 0.4171 \text{ mol/m}^3$

\[
\frac{r_{obs} \rho_p R_p n}{k_c C_{AB}^n}
= \frac{(5.571 \times 10^{-4} \frac{\text{mol}}{\text{kg}_{\text{cat}} \cdot \text{s}}) \times (1050 \frac{\text{kg}}{\text{m}^3}) \times (1.0675 \times 10^{-4} \text{ m}) \times 0.5}{(0.56 \frac{\text{m}}{\text{s}}) \times (0.4171 \frac{\text{mol}}{\text{m}^3})}

= 1.34 \times 10^{-4} < 0.15
\]

Therefore, external diffusion effect could be neglected during the kinetic experiments.
4. References


