

Electronic Supplementary Information

Hydrodeoxygenation of anisole to benzene over Fe₂P catalyst by a direct deoxygenation pathway

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1. Figures

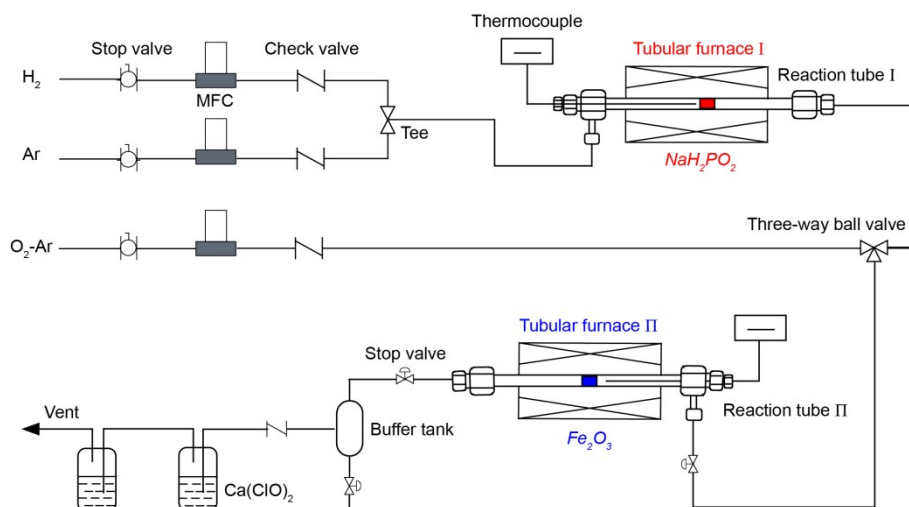


Fig. S1 Route for the synthesis of Fe₂P catalyst by a two-step phosphorization method. The first step is the reduction of Fe₂O₃ to α -Fe. The second step is heating the NaH₂PO₂ to produce PH₃ to phosphatize the α -Fe.

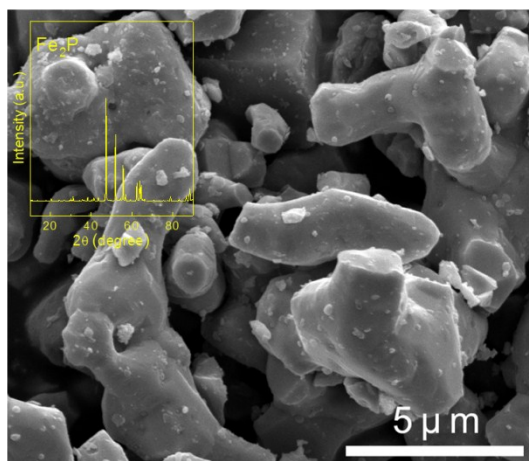


Fig. S2 SEM images and XRD patterns of Fe₂P prepared via TPR method.

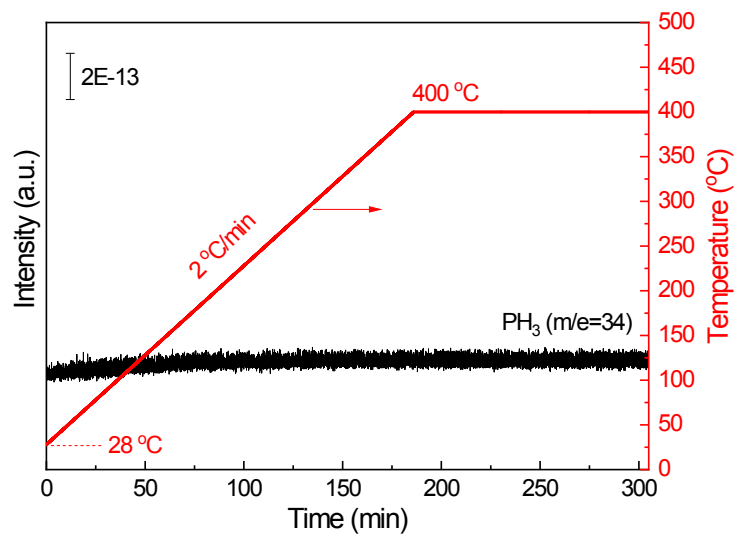


Fig. S3 MS signal of PH₃ (m/e = 34) during the reduction of Fe₂P catalyst.

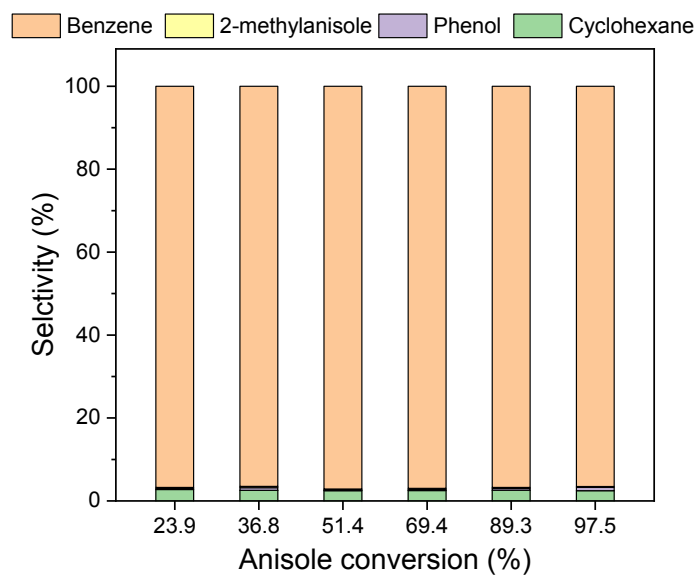


Fig. S4 Selectivity of benzene, 2-methylanisole, phenol and cyclohexane as a function of anisole conversion measured via different space time of anisole (200 °C, 0.1 MPa, H₂/anisole = 50).

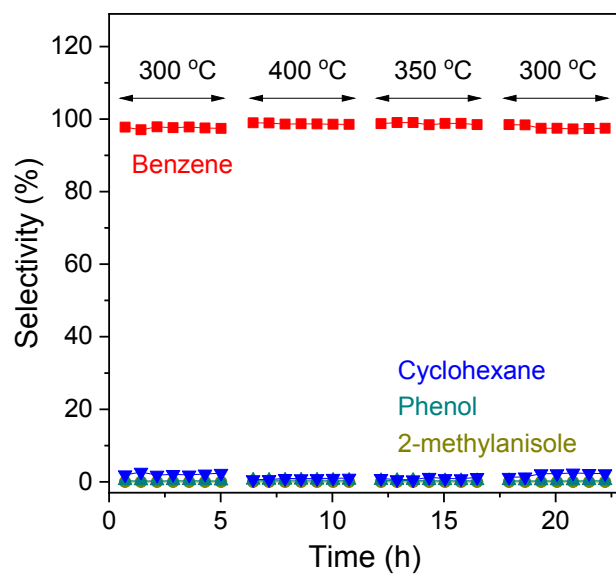


Fig. S5 Selectivity of benzene, 2-methylanisole, phenol and cyclohexane as a function of reaction temperature (0.1 MPa, $H_2/\text{anisole} = 50$, $WHSV = 1 \text{ h}^{-1}$).

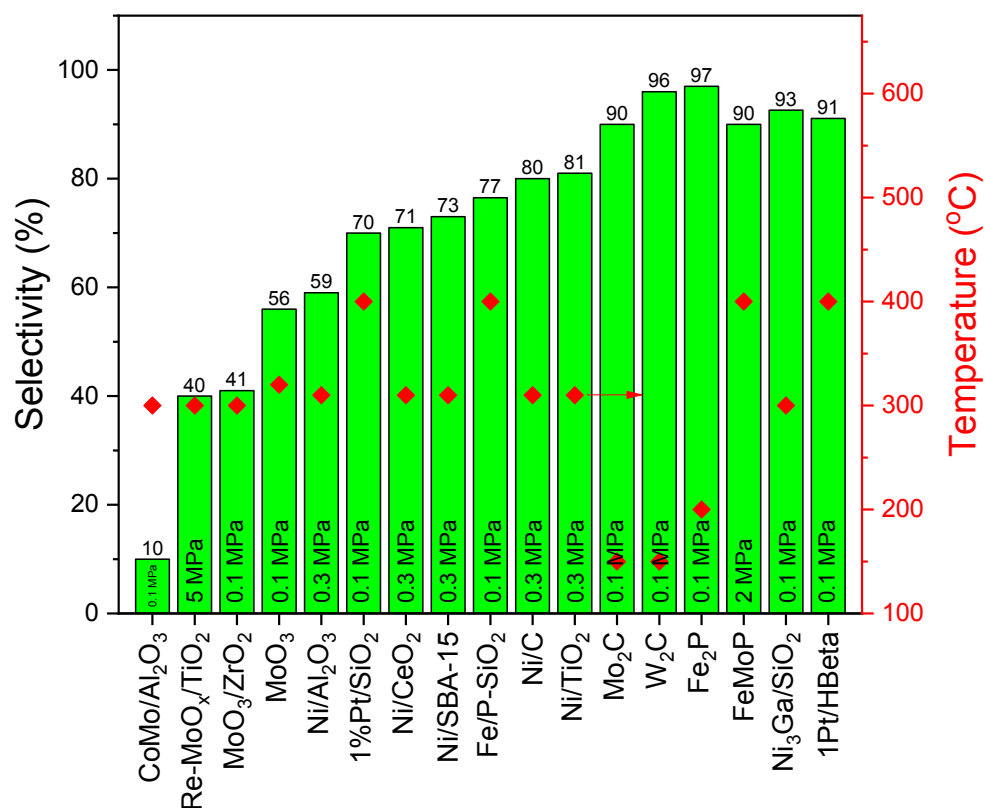


Fig. S6 The arene selectivity of different catalysts upon different evaluation conditions (temperature and pressure). The references are followed:

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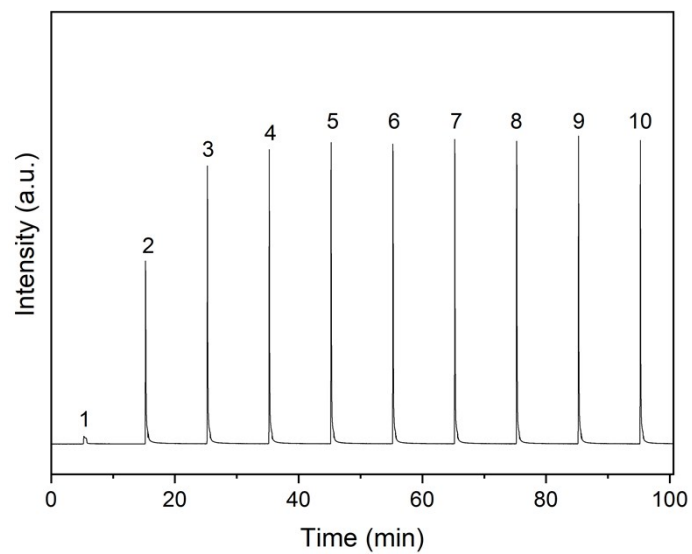


Fig. S7 Transient response curves of CO remained during pulse of 5.01%CO/He into pure He at 30 °C over the Fe₂P catalyst.

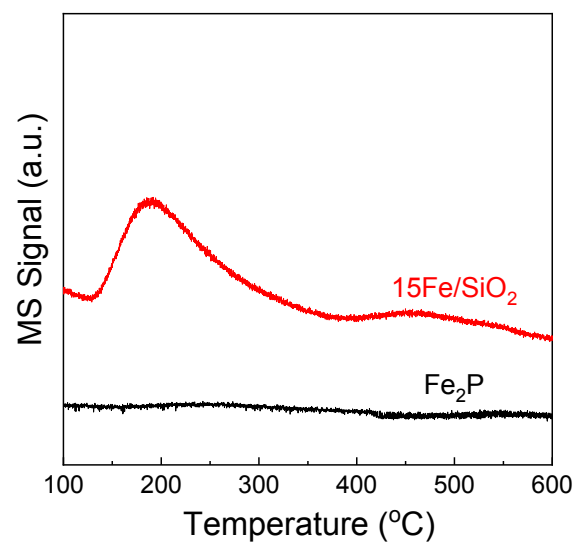


Fig. S8 Temperature-programmed desorption of ammonia over the Fe₂P and 15Fe/SiO₂ catalysts.

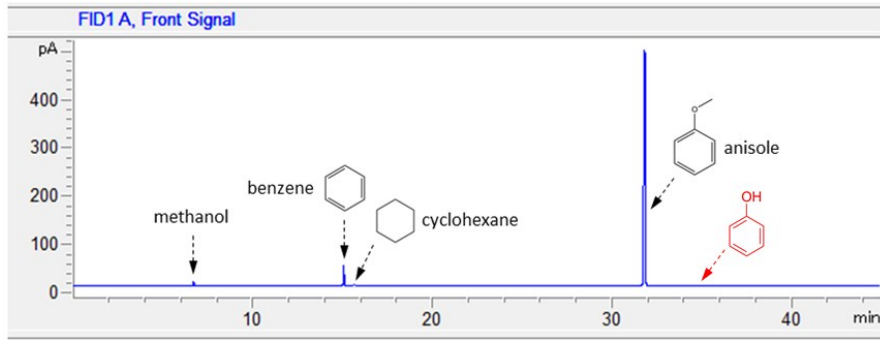


Fig. S9 Typical GC spectroscopy signals of hydrocarbons in tail gas. (Channel A with flame ionization detector (FID1 A)).

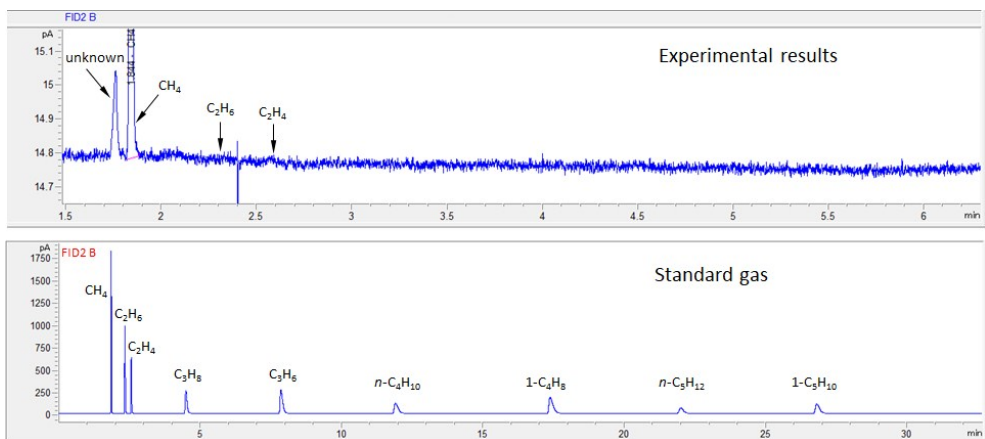


Fig. S10 Typical GC spectroscopy for hydrocarbons in tail gas. (Channel B with flame ionization detector (FID2 B)).

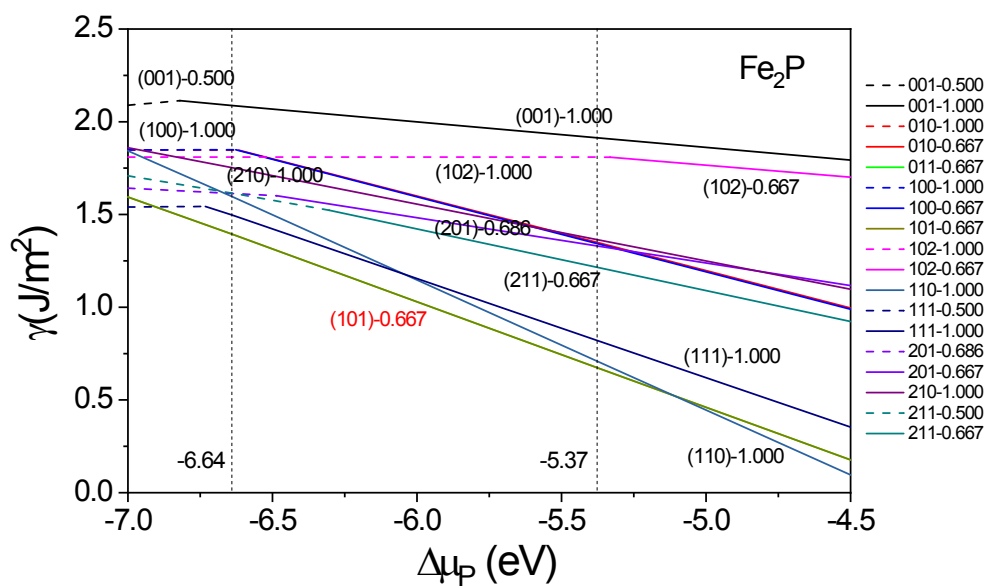


Fig. S11 Relationship of surface free energies of the most stable facets to $\Delta\mu$ (the boundary of $\mu = -5.37$ and -6.64 eV).

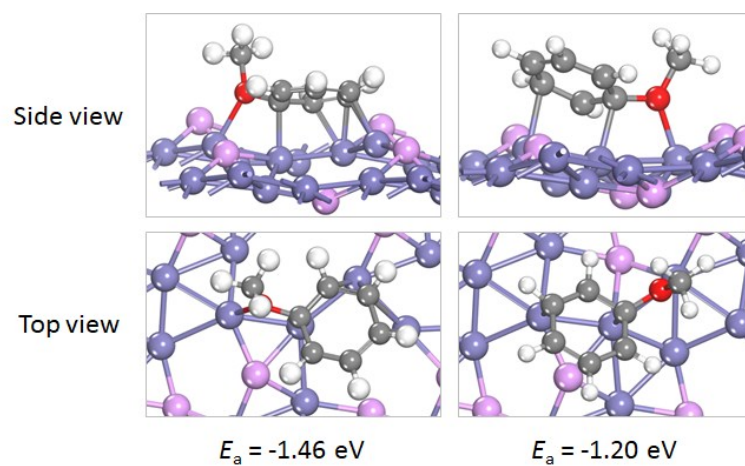


Fig. S12 Adsorption configurations and adsorption energies of anisole on Fe₂P(101) surface (Fe: blue, P: purple, C: gray, O: red, H: white).

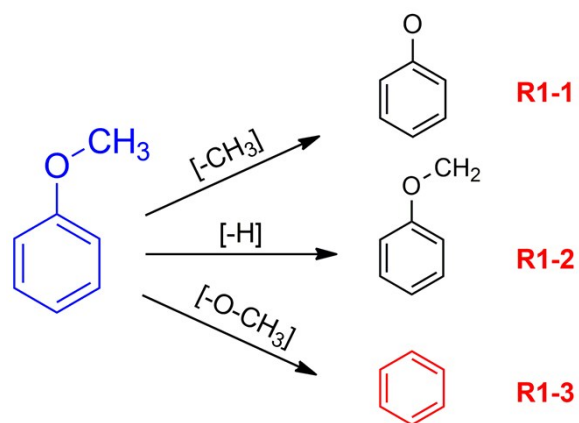


Fig. S13 Potential reaction pathways of anisole conversion.

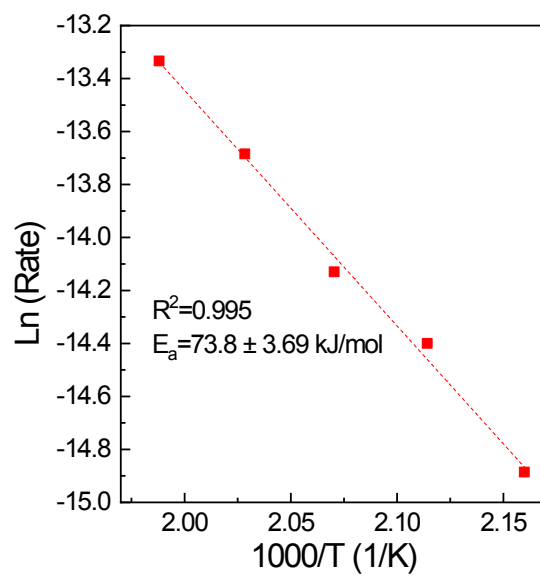


Fig. S14 Arrhenius plots of Fe₂P catalyst.

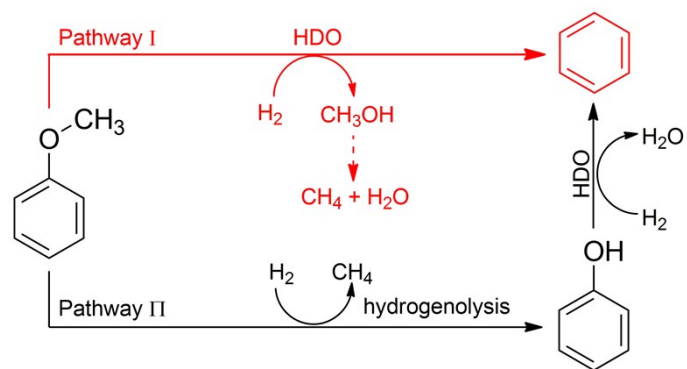


Fig. S15 Possible reaction pathway of anisole over Fe₂P catalyst.

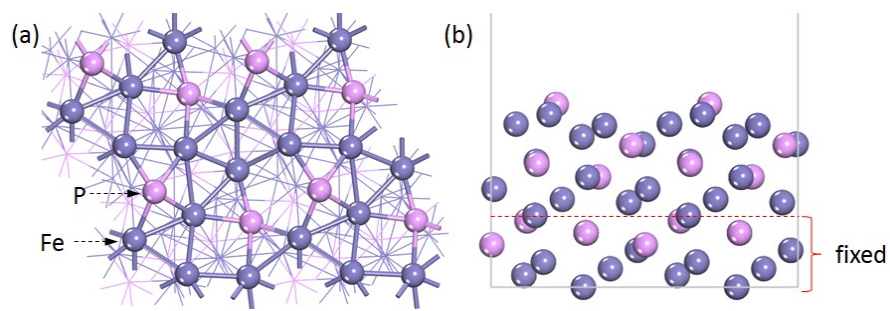


Fig. S16 Top (a) and side (b) view of $\text{Fe}_2\text{P}(101)$ surface.

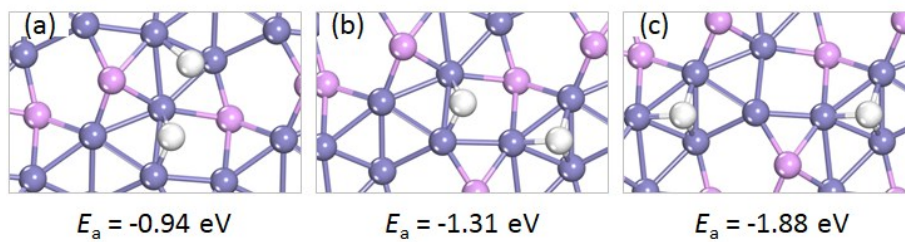


Fig. S17 Adsorption configurations and adsorption energies of H atoms on $\text{Fe}_2\text{P}(101)$ surface. Bri-bri (a), bri-hole (b) and hole-hole (c) configurations. (C: gray, O: red, H: white).

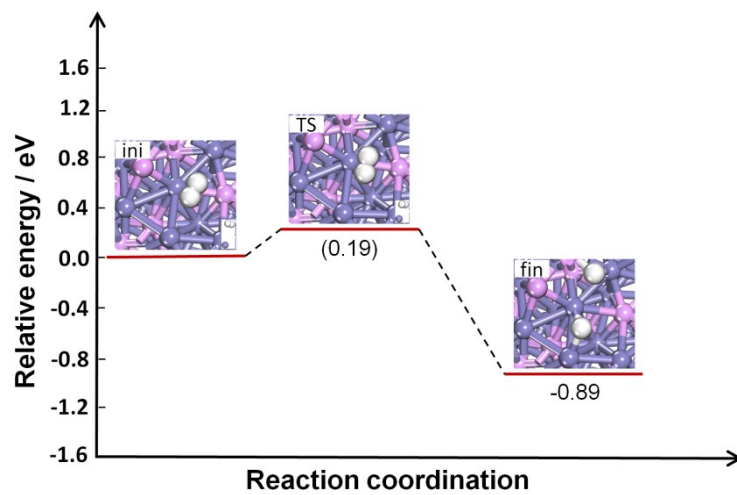


Fig. S18 Energy profiles of H₂ dissociation on the Fe₂P(101) surface and the correspond barrier is given in the parenthesis.

2. Tables

Table S1 XPS spectra of Fe2p of Fe₂P catalyst.

catalyst	relative concentration / %			
	fresh		spent	
	Fe ⁰	Fe ^{δ+}	Fe ⁰	Fe ^{δ+}
Fe ₂ P	46.9	53.1	73.0	27.0

3. Kinetic measurements

Kinetic measurements of vapor phase anisole hydrodeoxygenation on Fe₂P catalysts

(1) The absence of heat transfer was checked by Mears' criterion.^{1,2}

$$C_M = \left| \frac{-\Delta H r_{\text{obs}} \rho_b R E}{h T^2 R_g} \right|$$

Where ΔH = heat of reaction (for $C_7H_8O + H_2 \rightarrow C_6H_6 + CH_3OH$)

r_{obs} = observed reaction rate, kmol/kg_{cat}·s

ρ_b = density of catalyst bed, kg/m³

R = catalyst particle radius, m

E = activation energy, kJ/mol

h = heat transfer coefficient between gas and pellet, J/m²·s·K

R_g = gas constant, kJ/mol·K

T = reaction temperature, K

In the current work, a gas flow rate of 55.3 ml min⁻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 H₂ and anisole is 50:1).

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

$$Re = \frac{U \rho d_p}{\mu}$$

Where U = free-stream velocity, m/s

ρ = fluid density, kg/m³

d_p = diameter of pellet, m

μ = viscosity, kg/m·s

The viscosity is calculated according to the following formula:

$$\mu = (2.6693 \times 10^{-5}) \frac{\sqrt{MT}}{\sigma^2 \Omega_\mu}$$

Where M = molecular weight, g/mol

T = temperature, K

σ = collision diameter, Å

Ω_μ = collision integrals for use with the Lennard-Jones potential

Since $Re \ll 1$, heat transfer coefficient was estimated by assuming Nu (Nusselt number = $h \times d_p/k_t$) = 2, then:

$$Nu = \frac{hd_p}{k_t} \approx 2$$

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

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, $cal/mol \cdot K$

μ = viscosity, $kg/m \cdot s$

\tilde{C}_p = heat capacity $J/mol \cdot K$

For the Fe_2P catalyst,

$$T = 473.15 \text{ K}$$

$$Re = 5.689 \times 10^{-3}$$

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

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

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

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

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

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

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

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

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

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

$$\left| \frac{-\Delta H r_{obs} \rho_b R E}{h T^2 R_g} \right|$$

$$= \frac{(74.6 \frac{\text{kJ}}{\text{mol}}) \times (5.571 \times 10^{-7} \frac{\text{kmol}}{\text{kg}_{\text{cat}} \cdot \text{s}}) \times (1050 \frac{\text{kg}}{\text{m}^3}) \times (1.0675 \times 10^{-4} \text{ m}) \times (7.38 \times 10^4 \frac{\text{kJ}}{\text{kmol}})}{(2.424 \times 10^3 \frac{\text{J}}{\text{m}^2 \cdot \text{s} \cdot \text{K}}) \times (473.15 \text{ K})^2 \times (8.3145 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}})}$$

$$= 7.62 \times 10^{-8} < 0.15$$

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

$$C_{WP} = \frac{r_{\text{obs}} \rho_c R_p^2}{D_e C_s} < 1$$

Where r_{obs} = observed reaction rate, mol/kg_{cat}·s

ρ_c = density of catalyst pellet, kg/m³

R_p = catalyst particle radius, m

D_e = effective diffusivity, m²/s

C_s = gas concentration of A at the external surface of the catalyst, mol/m³.

C_s is gas concentration of A at the external surface of the catalyst in mol/m³. 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_{hep} is the pressure of anisole, atm

T = reaction temperature, K

R_g = universal gas constant, atm·cm³/mol·K

The average velocity for the anisole molecular is:

$$\bar{v} = \sqrt{\frac{8k_b T}{\pi m}}$$

Where k_b = the Boltzmann'n contant, 1.38×10^{-5} J/K

m = mass of anisole molecular

The mean free path in the gas phase is:

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \frac{N_{\text{anisole}}}{V}} = \frac{R_g T}{\sqrt{2}\pi\sigma^2 P_{\text{anisole}}}$$

Where σ = molecular diameter, 4.3×10^{-8} cm

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

$$D_e \approx D_{\text{Kn}} \left(D_{\text{Kn}} = \frac{\bar{v}\lambda}{3} \right)$$

For the Fe₂P catalyst,

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

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

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

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

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

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

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

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

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]

$$\text{MR} = \frac{r_{\text{obs}} \rho_c R_p n}{k_c C_{\text{Ab}}} < 0.15$$

Where r_{obs} = observed reaction rate, mol/kg_{cat}·s

ρ_c = density of catalyst pellet, kg/m³

R_p = catalyst particle radius, m

n = reaction order

k_c = external mass transfer coefficient, m/s

C_{Ab} = bulk gas concentration of A, mol/m³

For the H₂-anisole system, the diffusion coefficient of anisole is calculated based on the

following formula: [2]

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

$$\Omega_{AB} = \frac{1.06036}{T^{*0.15610}} + \frac{0.193}{e^{0.47635 \cdot T^*}} + \frac{1.03578}{e^{1.52996 \cdot T^*}} + \frac{1.76474}{e^{3.89411 \cdot T^*}}$$

Where D_{AB} = binary diffusion coefficient of A in B, m²/s

ϕ_p = pellet porosity

σ_c = constriction factor

$\tilde{\tau}$ = tortuosity

M_A = molecular weight of H₂, g/mol

M_B = molecular weight of anisole, g/mol

P = reaction pressure, atm

σ_{AB} = Lennard-Jones parameter, Å

Ω_{AB} = collision Integral

$$T^* = \frac{kT}{\varepsilon}$$

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, $Sc = \frac{\nu}{D_{AB}}$). Then,

$$Sh = \frac{k_c \times d_p}{D_{AB}} \approx 2$$

Where k_c = external mass transfer coefficient, m/s

d_p = diameter of pellet, m

For the Fe_2P catalyst,

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

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

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

$$n = 0.5$$

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

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

$$\frac{r_{\text{obs}} \rho_b R_p n}{k_c C_{\text{AB}}}$$

$$= \frac{(5.571 \times 10^{-4} \frac{\text{mol}}{\text{kg}_{\text{cat}} \cdot \text{s}}) \times (1050 \frac{\text{kg}}{\text{m}^3}) \times (1.0675 \times 10^{-4} \text{ m}) \times 0.5}{(0.56 \frac{\text{m}}{\text{s}}) \times (0.4171 \frac{\text{mol}}{\text{m}^3})}$$

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

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

4. References

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