Supplementary Information

Nickel and Cobalt phosphide as effective catalysts for oxygen-removal of dibenzofuran:

Role of contact time, hydrogen pressure and hydrogen/feed molar ratio

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In order to determine if internal diffusion is limiting the reaction the Weisz - Prater criterion can be used. It uses measured values of the rate of reaction to determine if the reaction suffers from problem of internal diffusion as follows:

$$C_{WP} = \frac{Actual\ reaction\ rate}{A\ diffusion\ rate} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{AS}} \qquad (1)$$

Internal mass transfer effect can be neglected when the value of C_{WP} is less than 1. The parameters used for the criterion are represented in Table 5.

Table S1. Experimental Parameters to calculate the C_{WP} parameter

R	Catalyst particle radius (cm)	0.05				
ρ_c	Solid catalyst density (g×cm^{-3})	0.25				
C_{AS}	Gas concentration at the catalyst surface (mol×cm^{-3})	P 30 bar H_2/DBF 69	P 15 bar H_2/DBF 69	P 1 bar H_2/DBF 69	P 30 bar H_2/DBF 34	P 30 bar H_2/DBF 139
		9.52×10^{-6}	4.76×10^{-6}	3.17×10^{-7}	1.89×10^{-5}	4.76×10^{-6}
D_e	Effective diffusivity (cm^2 × s^{-1})	Ni_2P			CoP	
		0.014			0.015	

The observed rates $-r'_A$ were calculated for each reaction carried out with equation (2):

$$-r'_{A=} \quad -\frac{\ln(1-X)}{\frac{W}{F}} \quad (mol\ s^{-1} g^{-1}) \qquad (2)$$

F_{DBF} is obtained by converting the volumetric flow rate ($\dot{v}$) into mass flow rate ($\dot{m}$) and then divide the mass flow rate with the molar mass of DBF:

$$\dot{m}(g\ min^{-1}) = \rho \times \dot{v} \quad (3)$$

$$F_{DBF}(mol\ min^{-1}) = \dot{m} / MW \quad (4)$$

The parameter C_{AS} is the gas concentration at the catalyst surface expressed in mol×cm^{-3}. The concentration of DBF at the surface is assumed to be equal to its bulk concentration:

$$C_{AS} = C_0 = N_{DBF}/V = P_{DBF}/RT \quad (5)$$

Example of calculation of C_{AS} (P 30 bar; H_2/DBF 69)

$$(30\ atm)(0.0143)/\left(\frac{82.06 atm \times cm^3}{g\ mole \times K}\right)(548.15) = \mathbf{9.52{\times}10^{-6}\ mol{\times}cm^{-3}}$$

The Effective diffusivity D_e in the criterion will in this case be substituted by Knudsen diffusion because the pore diameters (D_p) are between 16-18 nm and pore diffusion will therefore be dominated by Knudsen diffusion (D_{Kn}) and is calculated by fomula 17:

$$D_{Kn} = \frac{Vave \times Dp}{3} \quad (6)$$

Where V_{ave} is the average velocity for the DBF molecules. V_{ave} is calculated by the formula:

$$V_{ave} = [8k_BT/\pi m]^{0.5} \quad (7)$$

Where k_B is Boltzmann's constant and m is the mass of molecular species.

Example of calculation of V_{ave}:

$$V_{ave} = \left[\frac{8(1.38 \times 10^{-16} erg \times K^{-1})(548.15K)}{\pi(168.19 amu)(1.66 \times 10^{-24} g \times amu^{-1}}\right]^{0.5} = 2.62{\times}10^4\ cm\ s^{-1}$$

Finally D_{Kn} can be found applying formula 17. Example of calculation of D_{Kn} (Ni_2P catalyst):

$$D_{Kn} = \frac{2.62 \times 104\ cm\ s - 1\ \times\ (1.61 \times 10^{-6} cm)}{3} = 0.014\ cm^2\ s^{-1}$$

The observed rates $-r'_A$ for all of the reactions and corresponding Weisz –Prater Criterion are presented in the results[24][25].

Table S2 and S3 compile the observed reaction rates and corresponding Weisz-Prater criterion for Ni_2P and CoP catalyst are listed.

Table S2. The observed reaction rates and corresponding Weisz-Prater criterion for $Ni_2P/SiO2$

Pressure Bar	H_2/DBF ratio	Contact time / s	$-r'_{A(obs)}$ Observed reaction rate / mol g^{-1} s^{-1}	C_{WP} Weisz-Prater criterion
30	69.2	1.8	5.55 x10^{-7}	0.003
30	69.2	2.4	8.78 x10^{-7}	0.004
30	69.2	3.6	2.20 x10^{-6}	0.010
30	69.2	6.0	2.77 x10^{-6}	0.013
30	69.2	12	1.41 x10^{-6}	0.007
1	69.2	6	1.07 x10^{-7}	0.015
15	69.2	6	2.62 x10^{-6}	0.024
30	34.3	6	7.79 x10^{-6}	0.018
30	139.0	6	2.0 x10^{-6}	0.019

Table S3. The observed reaction rates and corresponding Weisz-Prater criterion for CoP/SiO2

Pressure Bar	H_2/DBF ratio	Contact time / s	$-r'_{A(obs)}$ Observed reaction rate / mol g^{-1} s^{-1}	C_{WP} Weisz-Prater criterion
30	69.2	1.8	1.22 x10^{-6}	0.005
30	69.2	2.4	8.33 x10^{-7}	0.004
30	69.2	3.6	5.14 x10^{-7}	0.002
30	69.2	6.0	7.99 x10^{-7}	0.003
30	69.2	12	1.16 x10^{-6}	0.005
1	69.2	6	5.07 x10^{-8}	0.007
15	69.2	6	9.37 x10^{-7}	0.008
30	34.3	6	1.10 x10^{-6}	0.002
30	139.0	6	1.07x10^{-6}	0.009

As previous described the internal mass transfer effects can be neglected when the value of C_{WP} is less than 1. All the values of C_{WP} are in the order of 10^{-2}-10^{-3}. This indicates that internal mass transfer effects can be neglected at the conditions employed for reactivity study in this project.

XPS

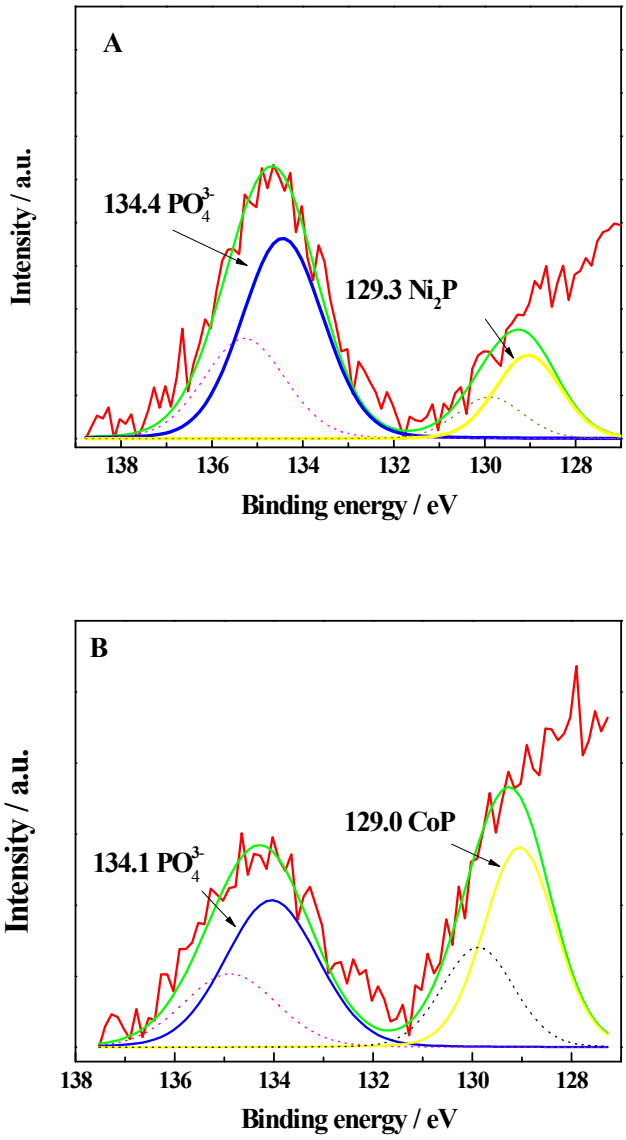

Figure S1. P 2*p* core level spectra for Ni_2P (A) and CoP (B) catalysts