Diagnosing Surface *versus* Bulk Reactivity for Molecular Catalysis within Metal-Organic Frameworks using a Quantitative Kinetic Model

Supporting Information

Ben A. Johnson* and Sascha Ott*

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, 751 20 Uppsala, Sweden

Email: ben.johnson@kemi.uu.se; sascha.ott@kemi.uu.se

Glossary of terms

Symbol	Meaning	Standard Units		
C_i	concentration of species <i>i</i>	mol cm ⁻³		
$C_{\rm cat}^0$	total concentration of catalyst or MOF loading	mol cm ⁻³		
$C_{\rm ox}^0$	solution concentration of oxidant	mol cm ⁻³		
$D_{\rm e}$	charge transport diffusion coefficient	cm ² s ⁻¹		
$D_{\rm ox}$	intra-MOF diffusion coefficient of freely diffusing oxidant	cm ² s ⁻¹		
$k_{\rm cat}$	observed first order catalytic rate constant	S ⁻¹		
k _d	second order rate constant for dimerization in I2M mechanism			
$k_{\rm ox}$	second order rate constant between catalyst and oxidant	cm ³ mol ⁻¹ s ⁻¹		
$k_{\rm ox}^{\rm s}$	second order heterogeneous rate constant between catalyst and cm ⁴ mol ⁻			
k_1	pseudo-first order rate constant for water nucleophilic attack step s			
k_2	first order rate constant for O ₂ release step	S ⁻¹		
$\overline{K_i}$	kinetic term for coupled chemical reactions of species <i>i</i>	mol cm ⁻³ s ⁻¹		
Ν	total number of MOF particles	n.a.		
R	MOF particle radius	cm		
r	radial distance from center of MOF particle			
S	surface area cm ²			
<i>TOF</i> ^{app}	apparent turnover frequency s ⁻¹			
TOF ^{true}	true turnover frequency s			
t	time			
$\delta_{ m rxn}$	reaction-diffusion layer thickness	cm		
v	overall observed rate of product (O ₂) formation	mol s ⁻¹		
\widetilde{K}_{ι}	dimensionless kinetic term for coupled chemical reactions of r			
8	dimensionless reaction diffusion layer thickness $-\delta$ /P	n 2		
0 A	dimensionless reaction-unusion ayer thickness $= \sigma_{rxn}/R$	n.a.		
U ĩ	dimensionless concentration of oxidant within MOF particle			
v ĩ	dimensionless concentration of species i	n ə		
l V	dimensionless radial distance from center of MOE particle	n a		
У		ii.a.		

Dimensionless Control Parameters

Symbol	Mechanism/Definition		Statement
λ	WNA	I2M	catalytic reaction rate
	$R^2 \frac{4k_{\rm cat}}{D_{\rm ox}} \frac{C_{\rm cat}^0}{C_{\rm ox}^0}$	$R^2 \frac{4k_2}{D_{\rm ox}} \frac{C_{\rm cat}^0}{C_{\rm ox}^0}$	physical diffusion rate of oxidant
μ	WNA $\frac{k_{cat}}{k_{ox}C_{ox}^{0}}$	I2M $\frac{k_2}{k_{\rm ox3}C_{\rm ox}^0}$	catalytic reaction rate oxidation reaction rate
$\sqrt{\frac{\lambda}{\mu}}$	WNA $R \sqrt{\frac{4k_{\rm ox}C_{\rm cat}^0}{D_{\rm ox}}}$	I2M $R\sqrt{\frac{2k_{\rm ox3}C_{\rm cat}^0}{D_{\rm ox}}}$	oxidation reaction rate physical diffusion rate of oxidant or particle radius reaction-diffusion layer thickness for oxidant
к	I2M $\frac{4k_{\rm d}C_{\rm cat}^0}{k_2}$		$\frac{\text{dimerization reaction rate}}{O_2 \text{ realease rate}}$
λ _e	WNA $R \sqrt{\frac{k_{\text{cat}}}{D_{\text{e}}}}$		catalytic reaction rateformal charge transport diffusion rateorparticle radiusreaction-diffusion layer thickness for charge transport
γ	WNA $R \frac{k_{\rm ox}^{\rm s} C_{\rm ox}^{\rm 0}}{D_{\rm e}}$		interfacial oxidation reaction rate formal charge transport diffusion rate
φ	Thiele modulus ⁵¹ $R\sqrt{\frac{k}{D}}$		reaction rate diffusion rate



Figure S1. Plot of dimensionless reaction rate $\tilde{v} = v/(N\pi RD_{ox}C_{ox}^0)$ as a function of $\mu = k_{cat}/(k_{ox}C_{ox}^0)$ when bulk reactivity is observed ($\lambda = 10^{-1}$), showing the transition from oxidant limited kinetics (zone I, large μ) to catalyst limited kinetics (zone III, small μ). The open circles are results from finite difference simulations and the solid black line is a plot of eq 6 from the main text (recalled below). This confirms the expression in eq 6 is valid for any value of μ as long as bulk reactivity holds ($\lambda \ll 1$). Vertical dotted line shows the transition between zones.

$$\tilde{v} = \frac{\lambda}{3(\mu+1)} - \frac{\mu\lambda^2}{45(\mu+1)^3}$$
 eq 6 (main text)



Figure S2. Plot of dimensionless reaction rate $\tilde{v} = v/(N\pi RD_{ox}C_{ox}^0)$ as a function of $\mu = k_{cat}/(k_{ox}C_{ox}^0)$ when surface reactivity is observed ($\lambda = 10^4$), showing the transition from oxidant limited kinetics (zone II, large μ) to catalyst limited kinetics (zone IV, small μ). The open circles are results from finite difference simulations and the solid black line is a plot of eq 7 from the main text (also see below). As $\mu \to \infty$, bulk reactivity with oxidant limited kinetics is recovered (zone I), and eq 7 is no longer valid. For $\mu > 10$, eq S.12 (dashed line) approximates the dimensionless rate under these conditions (zone I and II). Note the excellent agreement between these two expressions and the simulated results (open circles). Vertical dotted lines show transitions between zones.

(-)
$$\tilde{v} = \sqrt{2\lambda \left(1 - \mu \ln\left(\frac{\mu + 1}{\mu}\right)\right)}$$
 eq 7 (main text)
(--) $\tilde{v} = \sqrt{\lambda/\mu} \coth\left(\sqrt{\lambda/\mu}\right) - 1$ eq S.12

A. Freely Diffusing Oxidant within MOF pores

Here we consider the reaction-diffusion problem of a freely diffusing sacrificial oxidant [ox] (with concentration C_{ox}) coupled to chemical oxidation and OER catalysis by a molecular water oxidation catalyst immobilized in a MOF particle approximated as spherical with radius = R. For simplicity, it is assumed that the diffusivity of [ox] inside the MOF particle is constant and is invariant to changes in concentration (of either [ox] itself or catalytic intermediates). The partition coefficients are unity for permeation of both oxidant and water into the particle from solution. Further, electron hopping between the catalyst units is not considered presently and oxidation of the catalytic intermediates occurs only via chemical oxidation by [ox] with a second order rate constant, k_{ox} . A first order rate constant for O₂ release from the complex can be defined as k_2 . Fast coordination of a water molecule then usually closes the catalytic cycle. The molecular catalyst is assumed to be homogenously distributed inside the particle. The general form of the equations describing the time and space dependent behavior of the concentration of each species *i* is given by Fick's second law of diffusion with radial symmetry plus a kinetic term K_i , which is some function of the concentration of oxidant and/or catalytic intermediates, resulting from the coupled chemical reactions.

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) + K_i$$

For the immobile catalyst species, which are not free to diffuse within the particle, this can be further simplified to

$$\frac{\partial C_i}{\partial t} = K_i$$

However, it should be noted that the catalytic intermediate concentrations are still a function of the radial variable, r, because the term K_i is coupled to the concentration of diffusing oxidant. The coupled chemical reactions are expected to be fast compared to the timescale of the experiment, meaning there is no accumulation of oxidant within the particle. We also assume that product diffusion (O₂) in the MOF pores is significantly faster than the other diffusional processes in operation during catalysis, *i.e.*, intra-MOF oxidant diffusion. When these conditions are satisfied a steady-state situation will persist. As such the overall rate of product (O₂) formation (v) in mol s⁻¹ is given by the total molar flow of oxidant entering the particle (where S is the particle surface area, D_{ox} is the intra-particle diffusion coefficient of the oxidant, and N is the total number of particles):

$$v = NSD_{\rm ox} \frac{1}{4} \frac{\partial C_{\rm ox}}{\partial r} \Big|_{R} = N\pi R^2 D_{\rm ox} \frac{\partial C_{\rm ox}}{\partial r} \Big|_{R}$$

The molecular water oxidation catalysts can operate by either of two possible mechanisms inside the MOF matrix, depending on the average neighbor-to-neighbor distance. If the metal centers are relatively close to each other in the pores, it is possible that the bimolecular I2M mechanism operates, while if the distance between the metal centers is too large for them to interact in a bimolecular reaction, a WNA mechanism will follow. The formal kinetic models for both mechanisms are shown in the following sections.

A.1 Formal Reaction-Diffusion Kinetic Model for WNA Mechanism

$$A + ox \xrightarrow{k_{0x1}} B + red$$
$$B + ox \xrightarrow{k_{0x2}} C + red$$
$$C + ox \xrightarrow{k_{0x3}} D + red$$
$$D + H_2 O \xrightarrow{k_1} E$$
$$E + ox \xrightarrow{k_{0x4}} F + red$$
$$F + H_2 O \xrightarrow{k_2} A + O_2$$

Given that water is the solvent as well as the substrate, the concentration of H_2O is taken as constant throughout the particle, which gives the pseudo-first order rate constant k_1 . The reaction-diffusion equations become

$$\frac{\partial C_{\text{ox}}}{\partial t} = D_{\text{ox}} \left(\frac{\partial^2 C_{\text{ox}}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{\text{ox}}}{\partial r} \right) - k_{\text{ox1}} C_{\text{ox}} C_{\text{A}} - k_{\text{ox2}} C_{\text{ox}} C_{\text{B}} - k_{\text{ox3}} C_{\text{ox}} C_{\text{C}} - k_{\text{ox4}} C_{\text{ox}} C_{\text{E}}$$

$$\frac{\partial C_{\text{A}}}{\partial t} = -k_{\text{ox1}} C_{\text{ox}} C_{\text{A}} + k_2 C_{\text{F}}$$

$$\frac{\partial C_{\text{B}}}{\partial t} = k_{\text{ox1}} C_{\text{ox}} C_{\text{A}} - k_{\text{ox2}} C_{\text{ox}} C_{\text{B}}$$

$$\frac{\partial C_{\text{C}}}{\partial t} = k_{\text{ox2}} C_{\text{ox}} C_{\text{B}} - k_{\text{ox3}} C_{\text{ox}} C_{\text{C}}$$

$$\frac{\partial C_{\text{D}}}{\partial t} = k_{\text{ox3}} C_{\text{ox}} C_{\text{C}} - k_1 C_{\text{D}}$$

$$\frac{\partial C_{\text{E}}}{\partial t} = k_1 C_{\text{D}} - k_{\text{ox4}} C_{\text{ox}} C_{\text{E}}$$

$$\frac{\partial C_{\text{F}}}{\partial t} = k_{\text{ox4}} C_{\text{ox}} C_{\text{E}} - k_2 C_{\text{F}}$$

With the initial and boundary conditions as follows

$$t = 0, \ \forall r: \ C_{\text{ox}} = C_{\text{ox}}^{0}, C_{\text{B}} = 0, \ C_{\text{C}} = 0, \ C_{\text{D}} = 0, \ C_{\text{E}} = 0, \ C_{\text{F}} = 0, \ C_{\text{A}} = C_{\text{cat}}^{0}$$

$$t > 0, \ r = 0: \frac{\partial C_{\text{ox}}}{\partial r} = 0$$

$$t > 0, r = R: \ C_{\text{ox}} = C_{\text{ox}}^{0}, \frac{\partial C_{\text{A}}}{\partial r} = 0, \ \frac{\partial C_{\text{B}}}{\partial r} = 0, \ \frac{\partial C_{\text{C}}}{\partial r} = 0, \ \frac{\partial C_{\text{D}}}{\partial r} = 0, \ \frac{\partial C_{\text{E}}}{\partial r} = 0, \ \frac{\partial C_{\text{F}}}{\partial r} = 0$$

At the particle-solution interface (r = R), forced convection from stirring maintains a constant concentration of [ox], $C_{ox}(t, R) = C_{ox}^{0}$. Mass balance on the catalytic intermediates $\forall t$ and $\forall r$ gives

$$C_{\rm A} + C_{\rm B} + C_{\rm C} + C_{\rm D} + C_{\rm E} + C_{\rm F} = C_{\rm cat}^{0}$$
 (S.1)

Application of steady-state yields

$$D_{\text{ox}}\left(\frac{\partial^{2}C_{\text{ox}}}{\partial r^{2}} + \frac{2}{r}\frac{\partial C_{\text{ox}}}{\partial r}\right) = k_{\text{ox1}}C_{\text{ox}}C_{\text{A}} + k_{\text{ox2}}C_{\text{ox}}C_{\text{B}} + k_{\text{ox3}}C_{\text{ox}}C_{\text{C}} + k_{\text{ox4}}C_{\text{ox}}C_{\text{E}}$$

$$k_{\text{ox1}}C_{\text{ox}}C_{\text{A}} = k_{2}C_{\text{F}}$$

$$k_{\text{ox2}}C_{\text{ox}}C_{\text{B}} = k_{\text{ox1}}C_{\text{ox}}C_{\text{A}}$$

$$k_{\text{ox2}}C_{\text{ox}}C_{\text{C}} = k_{\text{ox2}}C_{\text{ox}}C_{\text{B}}$$

$$k_{1}C_{\text{D}} = k_{\text{ox3}}C_{\text{ox}}C_{\text{C}}$$

$$k_{\text{ox4}}C_{\text{ox}}C_{\text{E}} = k_{1}C_{\text{D}}$$

$$k_{2}C_{\text{F}} = k_{\text{ox4}}C_{\text{ox}}C_{\text{E}}$$
(S.2)

Solving this system of equations for $K_{ox} = k_{ox1}C_{ox}C_A + k_{ox2}C_{ox}C_B + k_{ox3}C_{ox}C_C + k_{ox4}C_{ox}C_E$ using eq S.1 gives

$$K_{\rm ox} = \frac{4C_{\rm ox}C_{\rm cat}^0}{\frac{C_{\rm ox}}{k_2} + \frac{C_{\rm ox}}{k_1} + \frac{1}{k_{\rm ox1}} + \frac{1}{k_{\rm ox2}} + \frac{1}{k_{\rm ox3}} + \frac{1}{k_{\rm ox4}}}$$
(S.3)

It is likely that one of the oxidation reactions is much slower than the rest, and we can write

$$\frac{1}{k_{\text{ox}}} = \frac{1}{k_{\text{ox1}}} + \frac{1}{k_{\text{ox2}}} + \frac{1}{k_{\text{ox3}}} + \frac{1}{k_{\text{ox4}}}$$
(S.4)

Substitution into eq S.2 yields

$$D_{\rm ox}\left(\frac{\partial^2 C_{\rm ox}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\rm ox}}{\partial r}\right) = \frac{4k_{\rm ox}C_{\rm ox}C_{\rm cat}^0}{\frac{k_{\rm ox}C_{\rm ox}}{k_2} + \frac{k_{\rm ox}C_{\rm ox}}{k_1} + 1}$$
(S.5)

Dimensional analysis by defining $\theta = \frac{c_{ox}}{c_{ox}^0}$, $\tilde{\iota} = \frac{c_i}{c_{cat}^0}$, $y = \frac{r}{R}$, results in two dimensionless control parameters:

$$\mu = \frac{k_{\text{cat}}}{k_{\text{ox}} C_{\text{ox}}^0} \qquad \qquad \lambda = R^2 \frac{4k_{\text{cat}}}{D_{\text{ox}}} \frac{C_{\text{cat}}^0}{C_{\text{ox}}^0}$$

where,

$$k_{\rm cat} = \frac{k_1 k_2}{k_1 + k_2} \tag{S.6}$$

After rearrangement,

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{R^2}{D_{\text{ox}}} \frac{4k_{\text{ox}} \theta C_{\text{cat}}^0}{k_{\text{ox}} C_{\text{ox}}^0 \theta \left(\frac{1}{k_2} + \frac{1}{k_1}\right) + 1}$$
$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{R^2}{D_{\text{ox}}} \frac{4k_{\text{ox}} \theta C_{\text{cat}}^0 \frac{1}{k_{\text{ox}} C_{\text{ox}}^0} \left(\frac{1}{k_2} + \frac{1}{k_1}\right)^{-1}}{\left[k_{\text{ox}} C_{\text{ox}}^0 \theta \left(\frac{1}{k_2} + \frac{1}{k_1}\right) + 1\right] \frac{1}{k_{\text{ox}} C_{\text{ox}}^0} \left(\frac{1}{k_2} + \frac{1}{k_1}\right)^{-1}}$$

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{R^2}{D_{\text{ox}}} \frac{4\theta \frac{C_{\text{cat}}^0}{C_{\text{ox}}^0} \left(\frac{1}{k_2} + \frac{1}{k_1}\right)^{-1}}{\left[\theta + \frac{1}{k_{\text{ox}} C_{\text{ox}}^0} \left(\frac{1}{k_2} + \frac{1}{k_1}\right)^{-1}\right]}$$
$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{C_{\text{cat}}^0}{C_{\text{ox}}^0} \frac{R^2}{D_{\text{ox}}} \frac{4k_1 k_2}{(k_1 + k_2)} \frac{\theta}{\left[\theta + \frac{k_1 k_2}{k_{\text{ox}} C_{\text{ox}}^0(k_1 + k_2)}\right]}$$

the equation to be solved becomes

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \lambda \frac{\theta}{\mu + \theta}$$
(S.7)

with the dimensionless reaction rate given by

$$\tilde{v} = \frac{v}{N\pi R D_{\rm ox} C_{\rm ox}^0} = \frac{\partial \theta}{\partial y}\Big|_1 \tag{S.8}$$

We can now define $\widetilde{K_{\theta}}$ (dimensionless version of K_{ox}) given below as

$$\widetilde{K_{\theta}} = \lambda \frac{\theta}{\mu + \theta} \tag{S.9}$$

which essentially reflects Michaelis-Menten type kinetics for the overall reaction as described in the main text. Reference models^{52,53} with approximate analytical solutions to related problems can be found in references S2 and S3.

Subcase WNA-1A: Oxidant limited kinetics ($\mu \gg 1$)

Since θ can only take values between zero and one, if $\mu \gg 1$ then eq S.7 further reduces to

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\lambda}{\mu} \theta \tag{S.10}$$

The oxidation step(s) become globally rate-limiting (*i.e.*, C_{ox}^0 is small). The coefficient of θ takes the form of the classical Thiele modulus:

$$\phi^2 = \frac{\lambda}{\mu} = R^2 \frac{4k_{\rm ox}C_{\rm cat}^0}{D_{\rm ox}}$$

Integration of (S.10) taking into account the appropriate boundary conditions^{S4} yields the dimensionless concentration profile:

$$\theta = \frac{1}{y} \frac{\sinh\left(\sqrt{\lambda/\mu} y\right)}{\sinh\left(\sqrt{\lambda/\mu}\right)}$$
(S.11)

The dimensionless reaction rate using eq S.8 is given by

$$\tilde{v} = \frac{\sqrt{\lambda/\mu} \cosh\left(\sqrt{\lambda/\mu}\right) - \sinh\left(\sqrt{\lambda/\mu}\right)}{\sinh\left(\sqrt{\lambda/\mu}\right)}$$
(S.12)

$$=\sqrt{\lambda/\mu} \coth\left(\sqrt{\lambda/\mu}\right) - 1$$

Two limiting situations can be reached depending on the dimensionless parameter $\sqrt{\lambda/\mu}$.

Zone I: Bulk reactivity (oxidant limited kinetics), $\sqrt{\lambda/\mu} \ll 1$

Diffusion is fast compared to the rate of reaction, and the oxidant concentration is $\theta \sim 1$ throughout the particle.

$$\tilde{v} = \frac{\lambda}{3\mu} \tag{S.13}$$

(zone I)

Zone II: Surface reactivity (oxidant limited kinetics), $\sqrt{\lambda/\mu} \gg 1$

The rate of reaction is fast compared to diffusion. Depletion of the oxidant occurs in a reaction layer near the particle-solution interface.

$$\tilde{v} = \sqrt{\lambda/\mu}$$
 (S.14)
(zone II)

Internal Effectiveness factor η for oxidant limited kinetics

Since this limiting behavior matches the Thiele model^{S1} for many reaction-diffusion systems in porous particles, an expression for the effectiveness factor η can be obtained.^{S4} Defined as the observed reaction rate divided by the maximum reaction rate if the entire volume of the particle were exposed to the surface conditions of the oxidant (C_{ox}^0), *i.e.*, when any diffusional gradients are absent and $\theta \sim 1$. For this we can use eq S.12 for the observed rate and eq S.13 for the maximum bulk reactivity rate.

$$\eta = \frac{\sqrt{\lambda/\mu} \coth\left(\sqrt{\lambda/\mu}\right) - 1}{\frac{\lambda}{3\mu}}$$
$$\eta = 3\frac{\mu}{\lambda} \left[\sqrt{\lambda/\mu} \coth\left(\sqrt{\lambda/\mu}\right) - 1\right]$$
(S.15)

A plot of η vs. $\sqrt{\lambda/\mu}$ using eq S.15, results in the curve shown in Figure 5 of the main text.

Subcase WNA-1B: Bulk reactivity approximation (negligible consumption of oxidant, $\lambda \ll 1$)

A derivation to a similar problem⁵⁵ provided a reference for the calculation of the flux $(\partial \theta / \partial y)$ in this limit.

In this limit the overall reaction is much slower compared to diffusion. This means $\lambda \ll 1$, and the oxidant concentration is approximately constant in the particle ($\theta \sim 1$). For the moment, μ can take any value (large or small). Since λ is very small we can consider it a regular perturbation and write an asymptotic expansion given by $\theta = \theta_0 + \lambda \theta_1 + \lambda^2 \theta_2 + \cdots$.^{S6} Then, rewriting eq S.7 as

$$\nabla^2 \theta = \lambda \frac{\theta}{\mu + \theta} \tag{S.16}$$

0(1) terms:

 $\nabla^2 \theta_0 = 0, \, \theta_0(1) = 1$ $\theta_0 = 1$ Substituting $\theta = 1 + \lambda \theta_1 + \lambda^2 \theta_2 + \cdots$ into eq S.16 gives $1 + \lambda \theta_1 + \lambda^2 \theta_2 + \cdots$

$$\nabla^{2}\lambda\theta_{1} + \nabla^{2}\lambda^{2}\theta_{2} + \dots = \lambda \frac{1 + \lambda \theta_{1} + \lambda \theta_{2} + \lambda}{\mu + 1 + \lambda \theta_{1} + \lambda^{2}\theta_{2} + \dots}$$

$$\text{using } \frac{1}{1+z} = 1 - z \text{ (for } z \ll 1\text{)}$$

$$= \left(\frac{\lambda}{\mu+1}\right) \left(\frac{1 + \lambda \theta_{1} + \lambda^{2}\theta_{2} + \dots}{1 + \frac{\lambda \theta_{1}}{\mu+1} + \frac{\lambda^{2}\theta_{2}}{\mu+1} + \dots}\right)$$

$$+ \dots$$

$$= \left(\frac{\lambda}{\mu+1}\right) \left(1 - \frac{\lambda\theta_1}{\mu+1} + \cdots\right) (1 + \lambda\theta_1 + \cdots)$$
$$= \frac{\lambda}{\mu+1} + \frac{\mu\lambda^2}{(\mu+1)^2} \theta_1 + \cdots$$

 $O(\lambda)$ terms:

$$\frac{1}{y^2} \frac{\partial}{\partial y} \left(y^2 \frac{\partial \theta_1}{\partial y} \right) = \frac{1}{\mu + 1}$$

$$\frac{\partial}{\partial y} \left(y^2 \frac{\partial \theta_1}{\partial y} \right) = \frac{y^2}{\mu + 1}$$

$$\int \partial \left(y^2 \frac{\partial \theta_1}{\partial y} \right) = \int \frac{y^2}{\mu + 1} \partial y$$

$$y^2 \frac{\partial \theta_1}{\partial y} = \frac{1}{3} \frac{y^3}{\mu + 1} + C_1; \frac{\partial \theta}{\partial y} \Big|_0 = 0; C_1 = 0; \frac{\partial \theta_1}{\partial y} = \frac{1}{3} \frac{y}{\mu + 1}$$

$$\int \partial \theta_1 = \int \frac{1}{3} \frac{y}{\mu + 1} \partial y$$

$$\theta_1 = \frac{y^2}{6(\mu + 1)} + C_2; \theta_1(1) = 0; C_2 = -\frac{1}{6(\mu + 1)}; \theta_1 = \frac{y^2 - 1}{6(\mu + 1)}$$

$$O(\lambda^2) \text{ terms:}$$

$$\frac{1}{2} \frac{\partial}{\partial y} \left(y^2 \frac{\partial \theta_2}{\partial y} \right) = -\frac{\mu}{2} \theta$$

$$\frac{1}{y^2} \frac{\partial y}{\partial y} \left(y - \frac{1}{\partial y} \right) = \frac{\mu y^2 (y^2 - 1)}{(\mu + 1)^3}$$
$$\frac{\partial}{\partial y} \left(y^2 \frac{\partial \theta_2}{\partial y} \right) = \frac{\mu y^2 (y^2 - 1)}{6(\mu + 1)^3}$$
$$\int \partial \left(y^2 \frac{\partial \theta_2}{\partial y} \right) = \int \frac{\mu y^2 (y^2 - 1)}{6(\mu + 1)^3} \partial y$$

$$y^{2} \frac{\partial \theta_{2}}{\partial y} = \left(\frac{\mu}{6(\mu+1)^{3}}\right) \left(\frac{y^{5}}{5} - \frac{y^{3}}{3} + C_{3}\right); \frac{\partial \theta}{\partial y}\Big|_{0} = 0; C_{3} = 0$$

$$\frac{\partial \theta_{2}}{\partial y} = \left(\frac{\mu}{6(\mu+1)^{3}}\right) \left(\frac{y^{3}}{5} - \frac{y}{3}\right)$$

$$\int \partial \theta_{2} = \int \left(\frac{\mu}{6(\mu+1)^{3}}\right) \left(\frac{y^{3}}{5} - \frac{y}{3}\right) \partial y$$

$$\theta_{2} = \frac{\mu(3y^{4} - 10y^{2} + C_{4})}{360(\mu+1)^{3}}; \theta_{2}(1) = 0; C_{4} = 7; \theta_{2} = \frac{\mu(3y^{4} - 10y^{2} + 7)}{360(\mu+1)^{3}}$$

Therefore the dimensionless concentration profile with error = $O(\lambda^3)$ is

$$\theta = 1 + \lambda \frac{y^2 - 1}{6(\mu + 1)} + \lambda^2 \frac{\mu(3y^4 - 10y^2 + 7)}{360(\mu + 1)^3}$$
(S.17)

with the dimensionless reaction rate using eq S.8 given by

$$\tilde{v} = \frac{\lambda}{3(\mu+1)} - \frac{\mu\lambda^2}{45(\mu+1)^3}$$
 (S.18)

The kinetic behavior of the system now depends on one dimensionless parameters (μ), where two further limits can be defined.

Zone III: Bulk reactivity (catalyst limited kinetics), $\mu \ll 1$

The oxidation reaction rate is much faster than the catalyst kinetics, as well as there being no diffusional limitations inside the particle. The overall reaction rate is determined by the catalytic reaction steps:

$$\tilde{v} = \frac{\lambda}{3} \tag{S.19}$$

(zone III)

Zone I: Bulk reactivity (oxidant limited kinetics), $\mu \gg 1$:

The oxidation reaction is now globally rate-limiting and zone I behavior is recovered, considering only, when $\sqrt{\lambda/\mu}$ is very small ($\lambda \ll 1$ and $\mu \gg 1$). Eq S.17 simplifies to

$$\tilde{\nu} = \frac{\lambda}{3\mu} \tag{S.20}$$

(zone I)

Subcase WNA-1C: Surface reactivity approximation (depletion of oxidant, $\lambda \gg 1$)

A derivation to a similar problem⁵⁵ provided a reference for the calculation of the flux $(\partial \theta / \partial y)$ in this limit.

In the opposite case as the one above, when the catalytic reaction is fast compared to diffusion ($\lambda \gg 1$), then the oxidant is depleted forming a boundary layer near the particle-solution interface.

If $\mu \sim 1$, then depending on the magnitude of θ , the overall reaction could switch from zeroth order kinetics with respect to oxidant near the particle surface (where $\theta \rightarrow 1$) to first order kinetics near the interior of the particle (where $\theta \rightarrow 0$). In this case, we will need to consider the size of the boundary layer that forms near the particle-solution interface.

Defining a new parameter $\varepsilon = \lambda^{-1}$, which approaches zero when $\lambda \gg 1$, we can then determine the dimensionless reaction-diffusion layer or boundary layer thickness, (where δ_{rxn} from the main text is expressed as $\delta = \delta_{rxn}/R$). Eq S16 becomes

$$\varepsilon \nabla^2 \theta = \frac{\theta}{\mu + \theta}$$

The balance of dominant terms is

$$\varepsilon \frac{\theta}{(\delta)^2} \sim \frac{\theta}{\mu + \theta}$$

For constant θ and μ , the right hand side is O(1), and consequently,

$$\frac{\varepsilon}{(\delta)^2} \sim 1$$

The boundary layer thickness is therefore,

$$\delta \sim \sqrt{\varepsilon}$$

Then it is possible to rescale the radial coordinate to δ .^{S7}

$$z = \frac{1 - y}{\delta} = \frac{1 - y}{\sqrt{\varepsilon}}$$
(S.21)

 $y = 1 - z\sqrt{\varepsilon}$, $dy = -dz\sqrt{\varepsilon}$, and the value of $\theta(y)$ inside the boundary layer is defined as $Y(z) \sim \theta(y)$. Substituting into (S.8) we have:

$$\frac{\partial^2 Y}{\partial z^2} - \frac{2\sqrt{\varepsilon}}{1 - z\sqrt{\varepsilon}} \frac{\partial Y}{\partial z} = \frac{Y}{\mu + Y}$$
(S.22)

with the boundary conditions: z = 0: Y = 1; and $z \ge \delta$: $Y \rightarrow 0$

Where now the solution for the inner region can be sought in the form of a regular asymptotic expansion⁵⁶ given by,

$$Y = Y_0 + \sqrt{\varepsilon}Y_1 + \varepsilon Y_2 + \dots$$

Substituting the expansion into eq S.22, and only looking at leading order O(1) terms results in

$$\frac{\partial^2 Y_0}{\partial z^2} = \frac{Y_0}{\mu + Y_0} \tag{S.23}$$

$$\frac{\partial Y_0}{\partial z} \left(\frac{\partial^2 Y_0}{\partial z^2} \right) = \frac{\partial Y_0}{\partial z} \left(\frac{Y_0}{\mu + Y_0} \right)$$
$$\int \frac{\partial}{\partial z} \left[\frac{1}{2} \left(\frac{\partial Y_0}{\partial z} \right)^2 \right] = \int \left(\frac{Y_0}{\mu + Y_0} \right) \partial Y_0 = \int \left(1 - \frac{\mu}{\mu + Y_0} \right) \partial Y_0$$

$$\frac{1}{2} \left(\frac{\partial Y_0}{\partial z}\right)^2 = Y_0 + C_1 - \mu [\ln(\mu + Y_0) + C_2]; \frac{\partial Y_0}{\partial z} \to 0 \text{ as } Y_0 \to 0, \text{ so } C_1 = 0, \text{ and } C_2 = -\ln\mu$$
$$\frac{\partial Y_0}{\partial z} = -\sqrt{2\left(Y_0 - \mu \ln\left(\frac{\mu + Y_0}{\mu}\right)\right)}$$

Coming back to the original coordinates using eq S.21,

$$\sqrt{\varepsilon} \frac{\partial \theta}{\partial y} \sim \sqrt{2\left(\theta - \mu \ln\left(\frac{\mu + \theta}{\mu}\right)\right)}$$
$$= \sqrt{2\lambda\left(\theta - \mu \ln\left(\frac{\mu + \theta}{\mu}\right)\right)}$$

 $\theta(1) = 1$, therefore

$$\left. \frac{\partial \theta}{\partial y} \right|_{1} = \sqrt{2\lambda \left(1 - \mu \ln \left(\frac{\mu + 1}{\mu} \right) \right)} + O(\sqrt{\varepsilon})$$

Since the observed reaction rate (eq S.8) is proportional to the flux of oxidant entering the particle at the particle-solution interface (y = 1), with error = $O(\sqrt{\varepsilon})$,

$$\tilde{v} = \sqrt{2\lambda \left(1 - \mu \ln\left(\frac{\mu + 1}{\mu}\right)\right)}$$
(S.24)

(zone II and IV)

Eq S.24 is valid when $\lambda \gg 1$. Two limits can be further defined.

Zone IV: Surface reactivity (catalyst limited kinetics)

Under catalyst limited kinetics, when $\mu \ll 1$, the expression in S.24 simplifies to

$$\tilde{v} = \sqrt{2\lambda}$$
 (S.25)
(zone IV)

Zone II: Surface reactivity (oxidant limited kinetics)

Under oxidant limited kinetics, when $\mu \gg 1$ zone II is recovered, and the expression in S.24 simplifies to

$$\tilde{v} = \sqrt{\lambda/\mu}$$
 (S.26) (zone II)

It should be noted that if μ is large enough so that $\sqrt{\lambda/\mu} \ll 1$, the system enters zone I (see Figure S2.

<u>Zone II</u>

With $\mu \gg 1$, eq S7 can be written as

$$\nabla^2 \theta = \frac{\lambda}{\mu} \theta$$

When λ/μ is very large, a boundary layer is formed, and the balance of dominant terms is given by,

$$\frac{\theta}{(\delta)^2} \sim \frac{\lambda}{\mu} \theta$$
$$\delta = \sqrt{\mu/\lambda}$$

therefore,

$$\delta_{\rm rxn} = \sqrt{\frac{D_{\rm ox}}{4k_{\rm ox}C_{\rm cat}^0}} \tag{S.27}$$

One way to approximate a solution for the inner region (the concentration profile inside the boundary layer), as in the previous section, is to rescale the radial coordinate to the predicted value for δ ,^{S7}

$$z = \frac{1 - y}{\delta} = \frac{1 - y}{\sqrt{\mu/\lambda}}$$

Looking at the value of $\theta(y)$ inside the boundary layer (*i.e.*, the inner region) given by $Y(z) \sim \theta(y)$,

$$\frac{\partial^2 Y}{\partial z^2} - \frac{2\sqrt{\mu/\lambda}}{1 - z\sqrt{\mu/\lambda}} \frac{\partial Y}{\partial z} = Y$$

Now the solution for the inner region can be sought in the form of a regular asymptotic expansion^{S6} given by, $Y = Y_0 + \sqrt{\varepsilon}Y_1 + \varepsilon Y_2 + ...$, with now $\varepsilon = \mu/\lambda$.

Substituting the expansion into the differential equation and focusing on the leading order terms gives,

$$\frac{\partial^2 Y_0}{\partial z^2} = Y_0, \quad Y_0(0) = 1$$

which results in the inner solution,

$$Y_0(z) = e^{-z}$$

Transforming back into the original coordinates gives,

$$\theta(y) \sim e^{\frac{-(1-y)}{\delta}} = e^{\frac{-(1-y)}{\sqrt{\mu/\lambda}}}$$
(S.28)

with error $= O(\sqrt{\varepsilon})$. The dimensionless reaction-diffusion layer for zone II is displayed in Figure S3 with the numerically generated concentration profile.



Figure S3. Simulated concentration profile of oxidant shown by solid black line ($\theta = C_{ox}(r)/C_{ox}^0$ and y = r/R) within the MOF particle under conditions leading to zone II (input parameters: $\lambda = 10^4$, $\mu = 10$, $\sqrt{\mu/\lambda} = 0.032$). The predicted concentration profile in the boundary layer given by $\theta = e^{\frac{-(1-y)}{\sqrt{\mu/\lambda}}}$ assuming $\delta = \sqrt{\mu/\lambda} = 0.032$ is displayed for comparison (blue dots) and agrees well with the simulated results.

Zone IV

From above, we saw that the boundary layer thickness in zone IV can be approximated as

$$\delta \sim \sqrt{\varepsilon} = \sqrt{1/\lambda}$$

and therefore,

$$\delta_{\rm rxn} \sim \sqrt{\frac{D_{\rm ox} C_{\rm ox}^0}{4k_{\rm cat} C_{\rm cat}^0}} \tag{S.29}$$

This can be checked by boundary layer analysis, which will yield the inner solution for the concentration profile of oxidant considering $\lambda \gg 1$ and $\mu \ll 1$ (valid for zone IV). Returning to eq S.23 with the same expansion ($Y = Y_0 + \sqrt{\varepsilon}Y_1 + \varepsilon Y_2 + ...$), if $\mu \ll 1$ and $Y_0 \gg \mu$, which is valid in the boundary layer for zone IV, this can be rewritten as

$$\frac{\partial^2 Y_0}{\partial z^2} = 1$$

 $Y_0(0) = 1$, and from eq S.25, $\frac{\partial Y_0}{\partial z}\Big|_0 = -\sqrt{2}$. Integration with these boundary conditions results in

$$Y_0 = \frac{z^2}{2} - \sqrt{2}z + 1 \tag{S.30}$$

 $O(\sqrt{\varepsilon})$ terms:

$$\sqrt{\varepsilon}\frac{\partial^2 Y_1}{\partial z^2} + \frac{\partial^2 Y_0}{\partial z^2} - \frac{2\sqrt{\varepsilon}}{1 - z\sqrt{\varepsilon}}\frac{\partial Y_0}{\partial z} = \frac{Y_0 + \sqrt{\varepsilon}Y_1}{\mu + Y_0 + \sqrt{\varepsilon}Y_1}$$

Expanding the $\frac{\partial Y_0}{\partial z}$ term gives,

$$\sqrt{\varepsilon}\frac{\partial^2 Y_1}{\partial z^2} + \frac{\partial^2 Y_0}{\partial z^2} - 2\sqrt{\varepsilon}(1 + z\sqrt{\varepsilon})\frac{\partial Y_0}{\partial z} = \frac{Y_0 + \sqrt{\varepsilon}Y_1}{\mu + Y_0 + \sqrt{\varepsilon}Y_1}$$

Keeping only the $O(\sqrt{\varepsilon})$ terms results in

$$\sqrt{\varepsilon}\frac{\partial^2 Y_1}{\partial z^2} + \frac{\partial^2 Y_0}{\partial z^2} - 2\sqrt{\varepsilon}\frac{\partial Y_0}{\partial z} = \frac{Y_0 + \sqrt{\varepsilon}Y_1}{\mu + Y_0 + \sqrt{\varepsilon}Y_1}$$

In the boundary layer $Y_0 + \sqrt{\varepsilon}Y_1 \gg \mu$, making the right hand side ≈ 1 . Substituting the previous result for Y_0 finally yields,

$$\frac{\partial^2 Y_1}{\partial z^2} = 2z - \sqrt{2}$$

Integrating with the boundary conditions, $\frac{\partial Y_1}{\partial z}\Big|_0 = 0$ and $Y_1(0) = 0$, the result is

$$Y_1 = \frac{z^3}{3} - \frac{\sqrt{2}}{2}z^2 \tag{S.31}$$

Substituting eqs S.29 and S.30 back into the expansion gives,

$$Y = \sqrt{\varepsilon} \frac{z^3}{3} + \left(\frac{1}{2} - \frac{\sqrt{2}}{2}\right) z^2 - \sqrt{2}z + 1 + O(\varepsilon)$$

In the original coordinate, the inner solution with error = $O(\varepsilon)$ for $\theta(y)$ in the boundary layer is (valid for $(1 - \delta) < y < 1$):

$$\theta = \lambda \frac{(1-y)^3}{3} + \left(\frac{\lambda}{2} - \frac{\sqrt{2\lambda}}{2}\right)(1-y)^2 - \sqrt{2\lambda}(1-y) + 1$$
(S.32)

The dimensionless reaction-diffusion layer for zone **IV** is displayed in Figure S4 with the numerically generated concentration profile. Eq S.32 is only valid where $\theta \gg \mu$, and thus becomes inaccurate near the edge of the boundary layer and into the center of the particle when $\theta \rightarrow 0$ and $\theta \ll \mu$. As can be seen from the simulated results in Figure S4, θ rapidly approaches zero outside the boundary layer and as $y \rightarrow 0$. This condition is not met with eq S.32, which clearly is not equal to zero as $y \rightarrow 0$ (*i.e.*, eq S.32 is not uniformly valid). A complimentary outer solution describing the particle center is required to fully describe the

concentration profile in zone IV, and thus δ_{rxn} for zone IV is only an estimate as indicated in Table 3 of the main text.



Figure S4. Simulated concentration profile of oxidant shown by solid black line ($\theta = C_{ox}(r)/C_{ox}^0$ and y = r/R) within the MOF particle under conditions leading to zone IV (input parameters: $\lambda = 10^4$, $\mu = 10^{-3}$, $1/\sqrt{\lambda} = 0.01$. The predicted concentration profile in the boundary layer given by eq S.32 with $\delta = 1/\sqrt{\lambda} = 0.01$ is displayed for comparison (blue dots; only shown for $(1 - \delta) < y < 1$). The deviation of eq S.32 from the simulated results can be seen near the edge of the boundary layer where θ approaches zero.

A.2 Formal Reaction-Diffusion Kinetic Model for I2M Mechanism

$$A + ox \xrightarrow{k_{0x1} (fast)} B + red$$
$$B + ox \xrightarrow{k_{0x2}} C + red$$
$$C + ox \xrightarrow{k_{0x3}} D + red$$
$$2D \xrightarrow{k_d} E$$
$$E + 2H_2O \xrightarrow{k_2} 2B + O_2$$

Given that water is the solvent as well as the substrate, the concentration of H_2O is taken as constant throughout the particle. The reaction-diffusion equations become

$$\frac{\partial C_{\text{ox}}}{\partial t} = D_{\text{ox}} \left(\frac{\partial^2 C_{\text{ox}}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{\text{ox}}}{\partial r} \right) - k_{\text{ox1}} C_{\text{ox}} C_{\text{A}} - k_{\text{ox2}} C_{\text{ox}} C_{\text{B}} - k_{\text{ox3}} C_{\text{ox}} C_{\text{C}}$$
$$\frac{\partial C_{\text{A}}}{\partial t} = -k_{\text{ox3}} C_{\text{ox}} C_{\text{A}} - k_{\text{ox2}} C_{\text{ox}} C_{\text{B}} + 2k_2 C_{\text{E}}$$
$$\frac{\partial C_{\text{C}}}{\partial t} = k_{\text{ox1}} C_{\text{ox}} C_{\text{A}} - k_{\text{ox2}} C_{\text{ox}} C_{\text{B}} + 2k_2 C_{\text{E}}$$
$$\frac{\partial C_{\text{D}}}{\partial t} = k_{\text{ox2}} C_{\text{ox}} C_{\text{B}} - k_{\text{ox3}} C_{\text{ox}} C_{\text{C}}$$
$$\frac{\partial C_{\text{D}}}{\partial t} = k_{\text{ox3}} C_{\text{ox}} C_{\text{C}} - 2k_{\text{d}} C_{\text{D}}^{2}$$
$$\frac{\partial C_{\text{E}}}{\partial t} = k_{\text{d}} C_{\text{D}}^{2} - k_{2} C_{\text{E}}$$

With the initial and boundary conditions as follows

$$t = 0, \ \forall r: C_{\text{ox}} = C_{\text{ox}}^0, C_{\text{B}} = 0, \ C_{\text{C}} = 0, \ C_{\text{D}} = 0, \ C_{\text{E}} = 0, \ C_{\text{A}} = C_{\text{cat}}^0$$
$$t > 0, \ r = 0: \frac{\partial C_{\text{ox}}}{\partial r} = 0$$
$$t > 0, \ r = R: \ C_{\text{ox}} = C_{\text{ox}}^0, \frac{\partial C_{\text{A}}}{\partial r} = 0, \ \frac{\partial C_{\text{B}}}{\partial r} = 0, \ \frac{\partial C_{\text{C}}}{\partial r} = 0, \ \frac{\partial C_{\text{D}}}{\partial r} = 0, \ \frac{\partial C_{\text{E}}}{\partial r} = 0$$

At the particle-solution interface (r = R), forced convection from stirring maintains a constant concentration of [ox], $C_{ox}(t, R) = C_{ox}^{0}$. Mass balance on the catalytic intermediates gives $\forall t$ and $\forall r$,

$$C_{\rm A} + C_{\rm B} + C_{\rm C} + C_{\rm D} + C_{\rm E} = C_{\rm cat}^0$$
 (S.33)

Application of steady-state (with $C_A \rightarrow 0$) yields

$$D_{\rm ox}\left(\frac{\partial^2 C_{\rm ox}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\rm ox}}{\partial r}\right) = k_{\rm ox1}C_{\rm ox}C_{\rm B} + k_{\rm ox3}C_{\rm ox}C_{\rm C}$$
(S.34)

 $2k_2C_{\rm E} = k_{\rm ox2}C_{\rm ox}C_{\rm B}$ $k_{\rm ox2}C_{\rm ox}C_{\rm B} = k_{\rm ox3}C_{\rm ox}C_{\rm C}$

$$k_{\text{ox3}}C_{\text{ox}}C_{\text{C}} = 2k_{\text{d}}C_{\text{D}}^{2}$$
$$k_{\text{d}}C_{\text{D}}^{2} = k_{2}C_{\text{E}}$$
$$C_{\text{B}} = \frac{2k_{\text{d}}C_{\text{D}}^{2}}{k_{\text{ox2}}C_{\text{ox}}}$$
$$C_{\text{C}} = \frac{2k_{\text{d}}C_{\text{D}}^{2}}{k_{\text{ox3}}C_{\text{ox}}}$$

$$C_{\rm E} = \frac{\kappa_{\rm d} c_{\rm D}}{k_2}$$

Substitution into eq S.33 gives

$$\frac{2k_{\rm d}C_{\rm D}^2}{k_{\rm ox2}C_{\rm ox}} + \frac{2k_{\rm d}C_{\rm D}^2}{k_{\rm ox3}C_{\rm ox}} + \frac{k_{\rm d}C_{\rm D}^2}{k_2} + C_{\rm D} - C_{\rm cat}^0 = 0$$

$$\left(\frac{2k_{\rm d}}{k_{\rm ox2}C_{\rm ox}} + \frac{2k_{\rm d}}{k_{\rm ox3}C_{\rm ox}} + \frac{k_{\rm d}}{k_2}\right)C_{\rm D}^2 + C_{\rm D} - C_{\rm cat}^0 = 0$$

$$\frac{k_{\rm d}}{k_2} \left[\frac{\frac{2k_2}{k_{\rm ox3}} \left(\frac{k_{\rm ox3}}{k_{\rm ox2}} + 1\right) + C_{\rm ox}}{C_{\rm ox}}\right]C_{\rm D}^2 + C_{\rm D} - C_{\rm cat}^0 = 0$$
(S.35)

Substitution into (S.34), we can write

$$D_{\rm ox}\left(\frac{\partial^2 C_{\rm ox}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\rm ox}}{\partial r}\right) = 4k_{\rm d}C_{\rm D}^{\ 2} \tag{S.36}$$

Dimensional analysis by defining $\theta = \frac{c_{Ce}}{c_{ox}^0}$, $\tilde{\iota} = \frac{c_i}{c_{cat}^0}$, $y = \frac{r}{R}$, results in four dimensionless control parameters:

$$\kappa = \frac{4k_{\rm d}C_{\rm cat}^0}{k_2}, \ \mu = \frac{2k_2}{k_{\rm ox3}C_{\rm ox}^0}, \ \lambda = R^2 \frac{4k_2}{D_{\rm ox}} \frac{C_{\rm cat}^0}{C_{\rm ox}^0}, \ \rho = \frac{k_{\rm ox3}}{k_{\rm ox2}}$$

Eq S.30 can be rewritten as

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\kappa \lambda}{4} \widetilde{D}^2$$
(S.37)

Additionally, (S.35) becomes

$$\frac{k_{\rm d}C_{\rm cat}^0}{k_2} \left[\frac{\frac{2k_2}{k_{\rm ox3}}C_{\rm ox}^0}{\theta} \left(\frac{k_{\rm ox3}}{k_{\rm ox2}} + 1 \right) + \theta}{\theta} \right] \widetilde{D}^2 + \widetilde{D} - 1 = \left[\frac{\kappa}{4} \left(\frac{\mu(\rho+1)+\theta}{\theta} \right) \right] \widetilde{D}^2 + \widetilde{D} - 1 = 0$$

Solving for \widetilde{D}^2 and substitution into eq S.37 finally yields,

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\lambda}{\kappa} \frac{\left(\sqrt{1 + \kappa \left(\frac{\mu(\rho+1) + \theta}{\theta}\right)} - 1\right)^2}{\left(\frac{\mu(\rho+1) + \theta}{\theta}\right)^2}$$
(5.38)

with the dimensionless reaction rate given by

$$\tilde{v} = \frac{v}{N\pi R D_{\rm ox} C_{\rm ox}^0} = \frac{\partial \theta}{\partial y} \Big|_1$$
(S.39)

The equation to be solved (eq S.38) is non-linear, making a closed-form solution difficult to obtain; however, we can use asymptotic analysis to look at the behavior in limiting situations by taking maximum or minimum values of the dimensionless control parameters. Firstly, it can be expected that $k_{ox2} \gg k_{ox3}$ so that $\rho \rightarrow 0$. This simplification gives,

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\lambda}{\kappa} \frac{\left(\sqrt{1 + \kappa \left(\frac{\mu + \theta}{\theta}\right)} - 1\right)^2}{\left(\frac{\mu + \theta}{\theta}\right)^2}$$
(S.40)

which is now a function of only three dimensionless parameters.

$$\kappa = \frac{4k_{\rm d}C_{\rm cat}^0}{k_2} \qquad \mu = \frac{2k_2}{k_{\rm ox3}C_{\rm ox}^0} \qquad \lambda = R^2 \frac{4k_2}{D_{\rm ox}} \frac{C_{\rm cat}^0}{C_{\rm ox}^0}$$

I2M-1: fast dimerization ($\kappa \rightarrow \infty$ and $\mu \kappa \rightarrow \infty$)

This behavior would correspond to when the dimerization step is unconditionally fast, and either the oxidation step(s) or the oxygen release step is rate-limiting. Then eq S.34 simplifies to

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \lambda \frac{\theta}{\mu + \theta}$$
(S.41)

We can now define $\widetilde{K_{\theta}}$ given below

$$\widetilde{K_{\theta}} = \lambda \frac{\theta}{\mu + \theta} \tag{S.42}$$

which essentially reflects Michaelis-Menten type kinetics for the overall reaction as described above for the WNA mechanism. The resulting expressions for the dimensionless reaction rate are independent of κ , and therefore, are the same as in the WNA mechanism for each limiting kinetic behavior; however, the definitions of the dimensionless control parameters λ and μ , as expressed above for I2M, now differ from that for WNA.

Subcase I2M-1A: oxidant limited kinetics ($\mu \gg 1$)

If $\mu \gg 1$ then eq S.41 further reduces to

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\lambda}{\mu} \theta \tag{S.43}$$

Here the oxidation step(s) become globally rate-limiting. The coefficient of θ takes the form of the classical Thiele modulus:

$$\phi^2 = \frac{\lambda}{\mu} = R^2 \frac{2k_{\rm ox3}C_{\rm cat}^0}{D_{\rm ox}}$$

The solution is the same as in WNA-1A. Integration of (S.43) taking into account the appropriate boundary conditions yields the dimensionless reaction rate

$$\tilde{v} = \sqrt{\lambda/\mu} \coth\left(\sqrt{\lambda/\mu}\right) - 1$$
 (S.44)

Two limiting situations can be reached depending on the dimensionless parameter $\sqrt{\lambda/\mu}$.

Bulk reactivity (oxidant limited kinetics), $\sqrt{\lambda/\mu} \ll 1$:

$$\tilde{\nu} = \frac{\lambda}{3\mu} \tag{S.45}$$

Surface reactivity (oxidant limited kinetics), $\sqrt{\lambda/\mu} \gg 1$:

$$\tilde{v} = \sqrt{\lambda/\mu}$$
 (S.46)

Subcase I2M-1B: Bulk reactivity approximation (negligible consumption of oxidant, $\lambda \ll 1$)

The solution is the same as in WNA-1B, with the dimensionless reaction rate given by

$$\tilde{v} = \frac{\lambda}{3(\mu+1)} - \frac{\mu\lambda^2}{45(\mu+1)^3}$$
(S.47)

The kinetic behavior of the system now depends on one dimensionless parameters (μ), where two further limits can be defined.

<u>Bulk reactivity (O₂ release limited kinetics), $\mu \ll 1$:</u>

$$\tilde{\nu} = \frac{\lambda}{3} \tag{S.48}$$

Bulk reactivity (oxidant limited kinetics), $\mu \gg 1$:

$$\tilde{\nu} = \frac{\lambda}{3\mu} \tag{S.49}$$

Subcase I2M-1C: Surface reactivity approximation (depletion of oxidant, $\lambda \gg 1$)

In the opposite case as the one above, when the catalytic reaction is fast compared to diffusion $(\lambda \gg 1)$, then the oxidant is depleted forming a boundary layer near the particle-solution interface. There are now two situations to consider.

If $\mu \sim 1$, then depending on the magnitude of θ , the overall reaction could switch from zeroth order kinetics with respect to oxidant near the particle surface (where $\theta \rightarrow 1$) to first order kinetics near the interior of the particle (where $\theta \rightarrow 0$). In this case, we will need to consider the size of the boundary layer that forms near the particle-solution interface.

The solution is the same as the WNA-1C subcase (eq S.24). The dimensionless reaction rate is given by

$$\tilde{v} = \sqrt{2\lambda \left(1 - \mu \ln\left(\frac{\mu + 1}{\mu}\right)\right)}$$
(S.50)

Surface reactivity (oxidant limited kinetics), $\mu \gg 1$:

If $\mu \gg 1$ subcase I2M-1A is recovered and the reaction is limited solely by the oxidation reaction.

$$\tilde{v} = \sqrt{\lambda/\mu}$$
 (S.51)

Surface reactivity (O₂ release limited kinetics), $\mu \ll 1$:

When $\mu \ll 1$, the O₂ release step is rate-determining, and the expression in S.50 simplifies to

$$\tilde{v} = \sqrt{2\lambda}$$
 (S.52)

I2M-2: fast O₂ release ($\kappa \rightarrow 0$)

When κ is much smaller than unity, this implies the oxygen release step is faster than the dimerization step. Then, depending on the magnitude of λ and μ several subcases are described below.

Subcase I2M-2A: oxidant limited kinetics ($\mu\kappa\gg1$)

If though, $\mu \kappa \gg 1$, the overall reaction displays oxidant limited kinetics (implies $\mu \to \infty$) and the I2M-1A subcase is recovered (see eq S.44).

$$\tilde{v} = \sqrt{\lambda/\mu} \coth\left(\sqrt{\lambda/\mu}\right) - 1$$
 (S.53)

Subcase I2M-2B: Bulk reactivity approximation (negligible consumption of oxidant)

However, if $\mu \kappa \ll 1$, then the dimerization reaction becomes the globally rate-determining chemical step, and the oxidation reaction steps are fast. In addition if the oxidant concentration is assumed to be nearly constant within the particle ($\theta \sim 1$), eq S.40 reduces to

$$\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\lambda \kappa}{4}$$
(S.54)

Bulk reactivity (dimerization limited kinetics), $\mu \ll \theta$ with $\theta \sim 1$

Integration of (S.54), taking into account the boundary conditions gives

$$\theta = \frac{\lambda \kappa}{24} (y^2 - 1) + 1$$

$$\tilde{v} = \frac{\lambda \kappa}{12}$$

$$v = \frac{4}{3} N \pi R^3 k_{\rm d} (C_{\rm cat}^0)^2$$
(S.56)

This result shows that the observed rate (v) in eq S.56 is second order in C_{cat}^0 , as expected if the dimerization step is globally rate-determining with bulk reactivity (due to fast diffusion and/or small particles). Other diagnostics for this limiting behavior include: proportionality of the observed rate to R^3 , and zero order kinetics with respect to C_{ox}^0 .

Subcase I2M-1C: Surface reactivity approximation (depletion of oxidant)

Here again we encounter a situation where the kinetics may be zero order with respect to the oxidant near the particle-solution interface; however, progressing outside the boundary layer into the interior of the particle, depletion of the oxidant causes the kinetics to switch to first order in oxidant. Taking $\kappa \to 0$ and $\mu \kappa \ll 1$ means the dimerization step will be globally rate-determining in the boundary layer where zeroth order kinetics in oxidant are observed. The second order character of the dimerization step quickly makes obtaining an approximate analytical solution intractable, even after applying asymptotic analysis as was done for the WNA mechanism. Although, it is clear that the overall observed rate will be some function of both κ and λ .

B. Oxidant size excluded from MOF pores: diffusional charge transport mechanism

In this situation the oxidant cannot diffuse through the particle, and rather a charge hopping mechanism carries holes into the interior of the framework. This charge hopping mechanism consist of a series of bimolecular self-exchange electron transfer reactions between the molecular catalysts within the framework, which is formally the diffusion of fixed redox centers.^{58,59} Therefore, the catalytic species is responsible for performing both charge propagation and catalysis. A heterogeneous reaction at the particle-solution interface between the oxidant and the molecular catalyst initiates charge transport within the particle. Diffusional charge transport can be described by an apparent diffusion coefficient D_e , which is taken as constant and is invariant to changes in redox state of the framework. The particle is approximated as spherical and the catalyst is homogeneously dispersed within the particle. A simplified mechanism for OER is examined (see main text and Figure 6 for detailed description), only considering WNA, where O-O bond formation is rate-limiting ($k_{cat} = 4k_1$). Water is the solvent and substrate, and its concentration is assumed constant as above. Additionally we assume O₂ diffusion inside the MOF is comparatively faster than diffusional charge transport and will not be limiting. The generalized reaction scheme is given below.

$$A|_{r=R} + ox|_{r=R} \xrightarrow{k_{ox}^{s}} B|_{r=R} + red|_{r=R}$$

(D_e) B + A \Rightarrow A + B
B + H₂O $\xrightarrow{k_{cat}} A + O_2$

The governing equations and boundary conditions are

$$\frac{r = 0}{\frac{\partial C_{B}}{\partial r}}\Big|_{r=0} = 0 \qquad \frac{\partial C_{A}}{\partial r}\Big|_{r=0} = 0$$

$$\frac{0 < r < R}{\frac{\partial C_{B}}{\partial t}} = D_{e}\left(\frac{\partial^{2}C_{B}}{\partial r^{2}} + \frac{2}{r}\frac{\partial C_{B}}{\partial r}\right) - k_{cat}C_{B}$$

$$\frac{\partial C_{A}}{\partial t} = D_{e}\left(\frac{\partial^{2}C_{A}}{\partial r^{2}} + \frac{2}{r}\frac{\partial C_{A}}{\partial r}\right) + k_{cat}C_{B}$$

$$C_{A} + C_{B} = C_{cat}^{0}$$

$$C_{ox} = 0$$

$$\frac{r = R}{\frac{\partial C_{B}}{\partial t}}\Big|_{r=R} = -D_{e}\frac{\partial C_{B}}{\partial r}\Big|_{r=R} + k_{ox}^{s}C_{ox}^{0}C_{A}^{r=R}$$
(S.58)

 $C_{\rm ox} = C_{\rm ox}^0, \ C_{\rm A} = 0, \ C_{\rm B} = 0$

When the coupled chemical reactions are fast compared to the timescale of the experiment, a steady-state situation will arise. Application of steady state to eq S.57 and eq S.58, focusing our attention on intermediate B, yields

$$D_{\rm e}\left(\frac{\partial^2 C_{\rm B}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\rm B}}{\partial r}\right) = k_{\rm cat}C_{\rm B}$$
(S.59)

$$D_{\rm e} \frac{\partial C_{\rm B}}{\partial r} \Big|_{r=R} = k_{\rm ox}^{\rm s} C_{\rm ox}^0 C_{\rm A}^{r=R}$$
(S.60)

With the overall observed rate now defined as the total flux of oxidized catalyst at the particle surface,

$$\nu = NSD_{\rm e} \frac{\partial C_{\rm B}}{\partial r}\Big|_{r=R} = 4N\pi R^2 D_{\rm e} \frac{\partial C_{\rm B}}{\partial r}\Big|_{r=R}$$
(S.61)

Dimensional analysis by defining $\tilde{\iota} = \frac{C_i}{C_{cat}^0}$, $y = \frac{r}{R}$, results in two dimensionless control parameters:

$$\lambda_e = R \sqrt{\frac{k_{\text{cat}}}{D_{\text{e}}}} \qquad \qquad \gamma = R \, \frac{k_{\text{ox}}^{\text{s}} C_{\text{ox}}^{\text{o}}}{D_{\text{e}}}$$

The equations to solve become:

$$\frac{\partial^2 \tilde{B}}{\partial y^2} + \frac{2}{y} \frac{\partial \tilde{B}}{\partial y} = \lambda_e^2 \tilde{B}$$
(S.62)

$$\left. \frac{\partial \tilde{B}}{\partial y} \right|_1 = \gamma \tilde{A}^{y=1} \tag{S.63}$$

with the dimensionless rate,

$$\tilde{v} = \frac{\partial \tilde{B}}{\partial y} \bigg|_{1} = \frac{v}{4N\pi R D_{\rm e} C_{\rm cat}^{0}}$$
(S.64)

Eq S.62 is readily solved resulting in the concentration profile and flux for \tilde{B} :

$$\left. \frac{\partial \tilde{B}}{\partial y} \right|_{1} = \tilde{B}^{y=1} (\lambda_{e} \coth \lambda_{e} - 1)$$
(S.65)

$$\tilde{B}(y) = \frac{\tilde{B}^{y=1}}{y} \frac{\sinh(\lambda_e y)}{\sinh(\lambda_e)}$$

Eq S.63 can be rewritten:

$$\tilde{v} = \frac{\partial \tilde{B}}{\partial y}\Big|_{1} = \gamma (1 - \tilde{B}^{y=1})$$
$$\tilde{B}^{y=1} = 1 - \frac{\tilde{v}}{\gamma}$$

Plugging this result into eq S.65 and solving for \tilde{v} yields the dimensionless expression for the rate.

$$\tilde{v} = \frac{\lambda_e \coth \lambda_e - 1}{1 + \frac{\lambda_e \coth \lambda_e - 1}{\gamma}}$$

$$\frac{1}{\tilde{v}} = \frac{1}{\gamma} + \frac{1}{\lambda_e \coth \lambda_e - 1}$$
(S.66)

Four limiting situations are straightforwardly obtained for large or small values of λ_e and γ . These are displayed in the zone diagram in Figure 10 of the main text.

Bulk reactivity $\lambda_e \rightarrow 0$:

Now the system depends on the single parameter $\frac{\lambda_e^2}{\gamma}$, giving

$$\frac{\lambda_e^2}{\gamma} \to \infty$$

$$\tilde{v} = \gamma$$
zone V(a)
$$\frac{\lambda_e^2}{\gamma} \to 0$$

$$\tilde{v} = \frac{\lambda_e^2}{2}$$
(S.67)

Surface reactivity $\lambda_e \rightarrow \infty$:

Now the system depends on the single parameter $\frac{\lambda_e}{\gamma}$, giving

$$\frac{\lambda_{e}}{\gamma} \rightarrow \infty$$

$$\tilde{v} = \gamma$$
zone V(b)
$$\frac{\lambda_{e}}{\gamma} \rightarrow 0$$

$$\tilde{v} = \lambda_{e}$$
zone VII
(S.70)

Reaction-diffusion layer (boundary layer) thickness $\delta=\delta_{ m rxn}/R$

Consider in the situation in zone **VII**, where $\lambda_e \to \infty$ and $\frac{\lambda_e}{\gamma} \to 0$, Eq S.62 can be written as

$$\nabla^2 \tilde{B} = \lambda_{\rm e}{}^2 \tilde{B}$$

The balance of dominant terms gives

$$\frac{\tilde{B}}{(\delta)^2} \sim \lambda_{\rm e}^2 \tilde{B}$$

$$\delta = \frac{1}{\lambda_{\rm e}}$$

$$\delta_{\rm rxn} = \sqrt{\frac{D_{\rm e}}{k_{\rm cat}}} \tag{S.71}$$

The boundary layer analysis for zone VII is identical to the situation in zone II, however; now with $\delta = \lambda_e^{-1}$:

$$\tilde{B}(y) \sim e^{\frac{-(1-y)}{\delta}} = e^{-\lambda_{e}(1-y)}$$
 (S.72)

valid for $\lambda_{\mathrm{e}} \gg 1$ and $rac{\lambda_{e}}{\gamma} \ll 1.$

C. MOF Structural Parameters

 $m_{\rm cat}$ = average number of catalyst sites per pore $n_{\rm cat}$ = total moles of catalyst used in catalytic assay (mol) $V_{\rm pore}$ = average pore volume (cm³) $V_{\rm cat} = V_{\rm pore}/m_{\rm cat}$ = average volume of pore per catalyst (cm³) N_A = 6.02x10²³ (mol⁻¹) $V_{\rm MOF}$ = MOF particle volume (= 4/3 πR^3) (cm³)

N = total number of MOF particles used in the catalytic assay

Calculation of v requires N and C_{cat}^0 , which are given by

$$N = \frac{n_{\text{cat}} N_A V_{\text{cat}}}{V_{\text{MOF}}} \quad C_{\text{cat}}^0 = \frac{n_{\text{cat}}}{V_{\text{MOF}} N} = (N_A V_{\text{cat}})^{-1}$$

D. Computational Details for Numerical Simulations

Finite difference method (FDM) was employed to numerically generate solutions (concentration profiles and fluxes) to the reaction-diffusion equation (eq S.7) due to the nonlinear kinetics of the coupled chemical reactions. Second order central differencing schemes for the first and second spatial derivatives were used on an uniform grid with a step size (Δy) of 0.001.^{S10} The flux of oxidant at the particle surface (y = 1) was computed using an asymmetric three-point discretization,^{S10} also second order (error = $O(\Delta y^2)$). A method of successive substitution^{S11} (or "relaxation method"^{S12}) was used to approximate the unknown non-linear term ($\widetilde{K_{\theta}}$) by assuming it is equal to an initial guess. The concentration at each grid point is calculated, which is then substituted into the linear system to approximate the nonlinear term in a successive iteration. This process is repeated until the solution converges to an acceptable tolerance (the average absolute difference for each grid point between successive iterations was $\leq 10^{-5}$).

E. References

- S1. E. W. Thiele, Ind. Eng. Chem., 1939, **31**, 916–920.
- M. E. G. Lyons, J. C. Greer, C. A. Fitzgerald, T. Bannon and P. N. Barlett, *Analyst*, 1996, 121, 715–731.
- S3. R. Swaminathan, K. Lakshmi Narayanan, V. Mohan, K. Saranya and L. Rajendran, *Int. J. Electrochem. Sci.*, 2019, **2019**, 3777–3791.
- S4. M. E. Davis and R. J. Davis, *Fundamentals of Chemical Reaction Engineering*, McGraw-Hill, New York, 1st edn., 2003.
- S5. M. Z. Bazant, Analysis of Transport Phenomena I: Mathematical Methods, https://www.edx.org/course/analysis-of-transport-phenomena-i-mathematical-met, (accessed December 2019), CC-BY-SA-3.0.
- S6. T. Witelski and M. Bowen, in *Methods of Mathematical Modelling*, Springer, 2015, Chapter 6–7, pp. 127–165.
- S7. M. M. Varma Arvind, in *Mathematical Methods in Chemical Engineering*, Oxford University Press, 1997, Chapter 9, pp. 611–648.
- C. P. Andrieux and J. M. Savéant, J. Electroanal. Chem. Interfacial Electrochem., 1980, 111, 377–381.
- S9. E. Laviron, J. Electroanal. Chem. Interfacial Electrochem., 1980, **112**, 1–9.
- S10. D. Britz and J. Strutwolf, *Digital Simulation in Electrochemistry*, Springer International Publishing, 4th edn., 2016.
- S11. S. C. Chapra, in *Applied Numerical Methods with MATLAB for Engineers and Scientists*, McGraw-Hill, New York, 3rd edn., 2012, pp. 633–635.
- S12. P. N. Bartlett and K. F. E. Pratt, J. Electroanal. Chem., 1995, 397, 61–78.