Diagnosing Surface Versus Bulk Reactivity for Molecular Catalysis Within Metal-Organic Frameworks Using a Quantitative Kinetic Model

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Submitted date: 07/05/2020 • Posted date: 08/05/2020
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Citation information: Johnson, Ben A; Ott, Sascha (2020): Diagnosing Surface Versus Bulk Reactivity for Molecular Catalysis Within Metal-Organic Frameworks Using a Quantitative Kinetic Model. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.12264110.v1

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

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Metal-organic frameworks (MOFs) are becoming increasingly popular as heterogenous support matrices for molecular catalysts. Given that reactants, or potentially holes/electrons, need to diffuse into the porous framework as the reaction proceeds, the reaction can possibly take place within the bulk of the particle or be confined to a thin layer at the surface due to transport limitations. Herein, a simple steady-state reaction-diffusion kinetic model is developed to diagnose these two mutually exclusive behaviors in MOF-based systems. The oxygen evolution reaction (OER) driven by a chemical oxidant is presented as an example mechanism. Quantitative metrics for assigning either bulk or surface reactivity are delineated over a wide variety of conditions, and numerical simulations are employed to verify these results. For each case, expressions for the turnover frequency (TOF) are outlined, and it is shown that surface reactivity can influence measured TOFs. Importantly, this report shows how to transition from surface to bulk reactivity and thus identifies which experimental parameters to target for optimizing the efficiency of MOF-based molecular catalyst systems.

Introduction

Metal-organic frameworks (MOFs) are rapidly being explored as potential catalysts for a variety of important chemical transformations. Their high internal surface area could indeed result in extraordinarily high concentration of active sites. Furthermore, incorporation of highly active and selective molecular catalysts into MOF structures, via a variety of post-synthetic methods,1,2 is possible due to the modularity of the organic linkers. This is advantageous as it can stabilize the molecular catalyst and avoid undesired bimolecular decomposition reactions, while providing a heterogeneous support matrix with a high density of anchoring sites. MOF-supported molecular catalysis has been previously demonstrated for energy related processes3-6 including proton reduction,7-9 CO₂ reduction,10-14 and water oxidation,15-20 as well as a variety of organic transformations with high-value products.21-25

However, given the interfacial nature of the reactions occurring in MOFs, mass and charge transport by a diffusional process are required to shuttle reactants, substrates, as well as electrons or holes to the molecular active sites in the MOF interior. As a result, situations arise where the catalytic reaction may be confined to the first few molecular layers or possibly even the surface of the particle. Determining where the reaction is occurring and what fraction of the imbedded molecular catalysts are active during the reaction is a prerequisite in order to take advantage of the high internal surface area displayed by MOF materials. Clearly, transport-limited or surface confined reactions would severely underutilize the large number of active sites within the MOF interior. Overcoming these limitations is of utmost importance not only to the efficiency but also to the performance (observed rate) and applicability of these materials to large-scale catalytic processes.26 Transport phenomena are often overlooked in kinetic studies of MOF-based catalysis. Indeed, only a handful of remarkable reports16,27-29 have accounted for these effects.30

Moreover, kinetic models integrating diffusional processes along with mechanistic details for the immobilized molecular catalysts are lacking. As a result, whether the reaction occurs exclusively near the surface of the particle due to transport limitations or throughout the bulk of the particle remains an open question for many MOF-catalysed reactions.

Choosing the oxygen evolution reaction (OER) driven by a (photo)chemical oxidant as an example, herein we develop a quantitative reaction-diffusion kinetic model to diagnose either surface or bulk reactivity occurring with a molecular catalyst homogeneously dispersed inside MOF particles. To the best of our knowledge, the present study is the first of its kind that summarizes the vast array of possible kinetic behaviours, and discusses means to distinguish between these different scenarios.

MOF-catalyst materials have been utilized extensively as micro-crystalline powders (particle sizes ranging from approximately 0.1 to 2 μm) suspended in solution. For energy related applications, a sacrificial chemical reagent (usually a strong oxidant or reductant) drives the reaction,16,18,29 or in a photochemical assay,9-11,14 a reducing or oxidizing photosensitizer is generated by quenching from a sacrificial donor or acceptor, respectively. In either case the oxidant or reductant must either physically diffuse through the pores or initiate a charge hopping process31,32 that delivers electrons or holes to the catalytic sites in the interior of the particles to generate the active form of the catalyst. It is well-known that such a charge hopping process is formally diffusional, obeying Fick’s laws.33,34 Therefore, regardless of the pore structure of the MOF, substrates, chemical reagents, and/or electrons or holes will need to diffuse through the particles as the catalytic reaction proceeds (relevant scenarios are shown in Figure 1). The resulting balance between reaction and diffusion will determine the surface vs. bulk reactivity of the MOF-catalyst construct (i.e., the location and size of the boundary layer in the particle where the reaction occurs) in addition to the overall rate.
vide infra, 19: 18 ding. n 2 via l forming reactions (hydrogen 38,40,41. As will be). the most. ations give. chanistic pathways. enoncentration of a specific reactant or the size of. 35,36. only to extract relevant kinetic data (rate constants and. these relationships. Furthermore, we use these diagnostic. criteria to illustrate how to assign the kinetic regime as either: 1) surface reactivity, or 2) bulk reactivity. This allows one not. diffusion coefficients) but to also identify which experimental. variables to change in order to optimize the system for the. highest efficiency and performance. Here, efficiency, commonly. quantified by the "effectiveness factor," is a measure of. catalyst utilization, i.e., what percentage of the immobilized. molecular catalysts within the MOF particle participate in the. reaction (vide infra). When diffusional transport limitations give. rise to surface reactivity, the efficiency of the MOF-catalyst will. become less than unity. Particular attention will be paid to the. contribution of catalyst oxidation/activation by the external. oxidant to the overall rate law. As will be shown, the. concentration of oxidant or holes (via charge hopping) may be. depleted within the particle significantly, which will decelerate. these reactions to the point where they become rate- determining. Furthermore, we demonstrate that different. values for the turnover frequency (TOF) can be obtained in the. limit of either surface reactivity or bulk reactivity. The scenario. where the oxidant can penetrate and diffuse into the MOF. pores is examined first, followed by the case where the pore. aperture size of the MOF is small and the oxidant is excluded. from entering the particle. In case of the latter, a heterogeneous. reaction at the particle-solution interface initiates the. diffusional charge hopping process that supplies holes to the. molecular catalyst.

The oxygen evolution reaction is used as an example; however, the fundamental principles of reaction-diffusion. arising in catalytic MOF particles outlined here for diagnosing. surface or bulk activity can be easily extended to other. mechanisms involving fuel forming reactions (hydrogen. evolution, CO₂ reduction) or a variety of catalytic organic. transformations where there exists a sacrificial or limiting. reactant.

Results and Discussion

(Phot)chemically driven OER.

Two mechanistic pathways (Figure 2) are most often proposed for molecular water oxidation catalysis: water nucleophilic. attack (WNA) and radical coupling (I2M). Additionally, the most. active molecular catalysts to-date are ruthenium-based. transition metal complexes, typically featuring polypyridyl. ligands.

Therefore, the two respective mechanisms. displayed in Figure 2, determined previously for homogeneous. Ru-based catalysts, will serve as the basis for the analysis. to follow considering reaction-diffusion when the molecular Ru- catalyst is incorporated into a MOF particle. These mechanisms. are also relevant, since there have been several previous. reports of molecular ruthenium catalyst incorporated into, for. example, the MIL-101(Cr) or UiO-67 frameworks, which. undergo OER in the presence of a chemical oxidant. There. are also several notable examples of Ir-based catalysts in UiO. frameworks. For brevity, only the WNA mechanism is. described in detail; although, as shown in the ESI, the I2M. mechanism exhibits the same general reaction-diffusion. behaviour. The latter is however less relevant in the context of. MOFs where the catalysts are often integral parts of the. material and will thus not engage in bimolecular encounters.
Oxidant diffusion through the MOF pores.

First we consider the situation where the aperture size of the MOF pores is sufficiently large to allow the oxidant (either a chemical oxidant or oxidized photosensitizer) to enter and diffuse through the MOF particles. The generalized reaction scheme for WNA is shown in Figure 3. The concentration of oxidant in the solution \( C_{\text{ox}}^0 \) is assumed to be constant over short times, i.e., when measuring initial rates. Wang et al. reported a reaction-diffusion model to account for consumption of the oxidant in the bathing solution over longer timescales \( (10-60 \text{ min}) \) in an experimental system with first order kinetics with respect to the oxidant. For the mechanisms displayed in Figure 2, we will see in the present treatment how the order of reaction with respect to the oxidant can switch from between first order and zero order depending on both \( C_{\text{ox}}^0 \) and the oxidant’s concentration gradient within the particle. The total concentration of catalyst in the particle is \( C_{\text{cat}}^0 \) (referred to as the “catalyst loading”), \( D_\text{ox} \) is the diffusion coefficient of the oxidant inside the MOF particle, \( R \) is the particle radius (approximated as spherical), \( N \) is the total number of individual MOF particles (see ESI for calculation of \( N \)), \( k_{\text{ox}} \) is the second order rate constant of the slowest oxidation reaction between the catalyst and oxidant (see ESI for derivation), \( k_1 \) is the pseudo-first order rate constant of the water nucleophilic attack step, and \( k_2 \) is the first order rate constant for the oxygen release step. Fast coordination of a water molecule follows the first order decay of the Ru\(^{II}\)-OO intermediate, which closes the catalytic cycle (Figure 3). The observed rate constant for the catalytic reaction steps (excluding the oxidation reactions to form the active catalyst) can be written as \( k_{\text{cat}} = (k_1 k_2)/(k_1 + k_2) \) in the case of WNA, where each step is first order with respect to the catalyst.

Applying steady-state, as shown in the ESI, the concentration of oxidant \( C_{\text{ox}}(r) \) within the particle is a function of the radial distance \( r \) (with \( r = 0 \) taken as the centre of the particle and \( r = R \) defined as the particle surface).

Two dimensionless parameters (\( \mu \) and \( \lambda \), Figure 3) control the resulting concentration profile of oxidant inside the particle as well as the observed rate of the reaction, \( v \) in mol s\(^{-1}\) (measured as the production of \( O_2 \)). The competition between the rate of the catalytic reaction \( (k_{\text{cat}}) \) and the rate of oxidation to form the catalytically active species is represented by \( \mu = k_{\text{cat}}/(k_{\text{ox}} C_{\text{ox}}^0) \). Importantly, \( \lambda = (4R^2 k_{\text{cat}}^0 C_{\text{ox}}^0)/D_\text{ox} C_{\text{ox}}^0 \) captures the influence of diffusion on the catalytic reaction and is defined as the ratio of the catalytic reaction rate to the diffusion rate of the oxidant inside the MOF particle.

Interestingly, the system of coupled reactions (Figure 3) results in kinetic behaviour that bears a strong resemblance to Michaelis-Menten kinetics as shown in the ESI, this is also the case for the I2M mechanism under certain conditions. At low concentrations, \( C_{\text{ox}}(r) \to 0 \), the reaction kinetics are first-order in oxidant. This shifts to zero-order with respect to \( C_{\text{ox}}(r) \) at higher “saturating” concentrations, at which point the reaction rate approaches a maximum value. Analogous to the Michaelis-Menten constant, the magnitude of \( \mu \) determines at what concentration of oxidant the system is “saturated.” This is shown in Figure 4a, which plots the dimensionless rate constant expression \( \theta \) as a function of the dimensionless oxidant concentration \( \theta(r) = C_{\text{ox}}(r)/C_{\text{ox}}^0 \) inside the particle. The saturating concentration of oxidant is indicated by the vertical dashed line where \( \mu = \theta(r) \) and the kinetics shift from first to zero-order.

\( \lambda = \frac{4R^2 k_{\text{cat}}^0 C_{\text{ox}}^0}{D_\text{ox} C_{\text{ox}}^0} \)

\( \mu = \frac{k_{\text{cat}}}{k_{\text{ox}} C_{\text{ox}}^0} \)

\( k_{\text{cat}} = \frac{k_1 k_2}{k_1 + k_2} \)

Figure 2. (a) Water nucleophilic attack (WNA) and (b) radical coupling (I2M) mechanisms for water oxidation by a ruthenium poly(pyridyl) catalyst driven with a (photo)chemical oxidant at pH = 1. The oxidized and reduced form of the oxidant are denoted by [ox] and [red] respectively.

Figure 3. Schematic diagram of MOF particle (top) with diffusing oxidant [ox] and generalized reaction scheme for WNA mechanism (bottom). As water is the solvent in addition to the substrate, its concentration is taken as large and constant both inside and outside the particle. Definitions of dimensionless governing parameters are given (top box).
Figure 4. (a) Plot of dimensionless kinetic term ($\bar{K}_\theta$), which represents the overall kinetics of the chemical reaction steps involving $\text{ox}$, as a function of the dimensionless concentration ($\theta = \frac{C_{\text{ox}}(r)}{C_{\text{ox}}^0}$, i.e., $\text{ox}$ normalized to its concentration in the bathing solution). The vertical line shows the value of $\mu$, which signals the change in reaction order in $\theta$ from first order to zero order. The horizontal line shows the maximum reaction rate set by $\lambda$. (b) Double logarithmic plot of $\bar{K}_\theta$ vs. $\theta$ for increasing values of $C_{\text{ox}}^0$ (black: $\lambda = 250$, $\mu = 10$; red: $\lambda = 25$, $\mu = 1$; blue: $\lambda = 2.5$, $\mu = 0.1$; green: $\lambda = 0.25$, $\mu = 0.01$; in all cases: $\lambda/\mu = 5$).

As $\theta(r) \rightarrow 1$, the rate approaches a maximum value (Figure 4a, horizontal dashed line), which is approximately equal to the magnitude of $\lambda$ (representing the intrinsic rate of the OER reaction attenuated by any interference from diffusion). If the solution oxidant concentration $C_{\text{ox}}^0$ is increased significantly, for nearly all values of $\theta(r)$ the reaction kinetics become saturated or zero-order in oxidant (Figure 4b, green line).

Approximate analytical solutions for the observed reaction rate ($v$), accounting for mass transport and the intrinsic kinetics of the oxidant/catalyst inside the MOF particle, can be obtained in various limiting situations by taking maximum or minimum values of the two dimensionless control parameters, $\lambda$ and $\mu$. For reference, each specific behaviour is assigned a zone (I to IV) with a corresponding closed-form expression for the observed rate. Numerical simulations are used to confirm the validity of the rate expressions.

**Oxidant limited kinetics.** We consider first the situation encountered when $\mu \gg 1$. This entails that $C_{\text{ox}}^0$ is low enough so the rate of oxidation of the catalyst is unconditionally slower than the catalytic reaction ($k_{\text{cat}}C_{\text{ox}}^0 < k_\text{cat}$). The overall kinetics of the system now depends only on a single dimensionless parameter $\sqrt{\lambda/\mu}$, which takes the form of the classical Thiele modulus (eq 1).

$$\sqrt{\frac{\lambda}{\mu}} = R \left( \frac{4k_{\text{cat}}C_{\text{cat}}^0}{D_{\text{ox}}} \right)$$

Regardless of the local concentration of oxidant, the kinetics are “unsaturated” throughout the particle (for all values of $r$) and first order with respect to $C_{\text{ox}}(r)$ (see Figure 4b, black line).

Two limits can be found depending on the magnitude of $\sqrt{\lambda/\mu}$. When the activation of the catalyst by the oxidant, which is now the globally rate-determining chemical step, is slow compared to its diffusion rate through the MOF particle (reaction-controlled: $\sqrt{\lambda/\mu} \ll 1$), bulk reactivity is observed, and the oxidant is present at a nearly constant concentration throughout the particle approximately equal to its value in the bathing solution. The observed rate is trivially (zone I)

$$v = \frac{4}{3} N \pi R^3 k_{\text{cat}} C_{\text{cat}}^0 C_{\text{ox}}^0$$

where $N$ is the total number of MOF particles. On the other hand, if oxidation of the catalyst is much faster than the diffusion time of the oxidant (transport-controlled: $\sqrt{\lambda/\mu} \gg 1$), the overall rate becomes

$$v = N \pi R^3 C_{\text{ox}}^0 \sqrt{D_{\text{ox}}/4k_{\text{cat}}^0 C_{\text{cat}}^0}$$

In this regime (zone II), $C_{\text{ox}}(r)$ is depleted near the particle surface, due to its fast consumption before the oxidant is able to diffuse into the centre of the particle. A boundary or reaction-diffusion layer is formed near the surface, with a thickness given by $\delta_{\text{rxn}} = \sqrt{D_{\text{ox}}/4k_{\text{cat}}^0 C_{\text{cat}}^0}$. Only catalytic sites contained within this thin layer are active, demonstrating surface reactivity as $\delta_{\text{rxn}}$ approaches the size of a monolayer. Using this definition of the boundary layer thickness, another way to characterize bulk reactivity is when the reaction-diffusion layer is equal to or larger than the particle size ($\sqrt{D_{\text{ox}}/4k_{\text{cat}}^0 C_{\text{cat}}^0} \geq R$). And in fact, $\sqrt{\lambda/\mu}$ is simply the ratio of these two length scales, i.e., $\sqrt{\lambda/\mu} = R/\delta_{\text{rxn}}$.

These two behaviors can be easily differentiated experimentally by plotting the observed reaction rate ($v$) as a function of the catalyst loading ($C_{\text{cat}}$) or the particle size ($R$). For bulk reactivity (zone I), a plot of $v$ vs. $C_{\text{cat}}^0$ gives a linear relationship and indicates that the reaction is occurring throughout the particle. Whereas $v$ vs. $\sqrt{C_{\text{cat}}^0}$ will be linear if the kinetics are controlled by transport and the reaction is contained near the particle surface (zone II). Similarly as expected, in the bulk reactivity regime the rate is proportional to $R^3$, indicating a dependence on the MOF particle’s volume. When transport limitations are present, the observed rate will display proportionality to $R^2$, or the surface area of the particle.

In either case, the rate-determining chemical step is first order in $C_{\text{ox}}(r)$ ($\mu \gg 1$), making $v$ linearly proportional to $C_{\text{ox}}^0$ under both bulk reactivity (reaction-controlled) and surface reactivity (transport-controlled) conditions. These diagnostic relationships are summarized in Table 1 using the order of the reaction rate with respect to each experimental variable.

The efficiency $\eta$, canonically referred to as the internal effectiveness factor, is defined as the ratio of the observed reaction rate to the maximum reaction rate ($eq 2$) in the absence of any diffusion gradients (see ESI eq S.15 for further details).
\[ \lambda / \mu = R \sqrt{4k_{\text{cat}}C_{\text{cat}}^0/D_{\text{ox}}} = R/\delta_{\text{rxn}} \]

This is a direct metric of how much of the catalyst is utilized or active in the reaction, as transport limitations fundamentally create boundary layers near the particle surface, outside of which the active catalyst concentration is essentially zero. Thus the primary effect of comparatively slow diffusion (when \( \sqrt{\lambda/\mu} \) is large) is that the total amount of catalyst participating in the reaction at steady-state – i.e., slow diffusion induces surface reactivity (\( \eta \ll 1 \) for surface reactivity, Figure 5 zone II; \( \eta = 1 \) for bulk reactivity, Figure 5 zone I). This in indeed a function of the particle size, since the oxidant will have a longer characteristic diffusion time \( t_{\text{diff}} \sim R^2/D_{\text{ox}} \) in particles with larger radii. The catalytic efficiency (or effectiveness factor) of the MOF particle as it varies with \( R \) is shown in Figure 5.

**Catalyst limited kinetics.** In the opposite limit, when \( \mu \ll 1 \) or under saturated kinetics, the catalytic reaction step(s) become globally rate-determining \( (k_{\text{ox}}C_{\text{ox}}^0 \gg k_{\text{cat}}) \). Either surface or bulk reactivity will dominate depending on the magnitude of \( \lambda \). First, as \( \lambda \ll 1 \), the catalytic reaction is much slower than diffusion, and there is minimal depletion of oxidant within the film. The reaction rate straightforwardly is given by eq 4 (zone III; Figure 6).

\[ v = \frac{4}{3} N\pi R^3k_{\text{cat}}C_{\text{cat}}^0 \]  

\[ v = \frac{4}{3} N\pi R^3k_{\text{cat}}C_{\text{cat}}^0 \]  

**Figure 5.** Internal effectiveness factor \( \eta \) plotted as a function of the dimensionless control parameter \( \sqrt{\lambda/\mu} \) relating the oxidant reaction kinetics to its rate of diffusion through the particle (oxidant limited kinetics, \( \mu \gg 1 \)). Bulk reactivity (zone I) with 100% active catalyst is observed when \( \eta = 1 \). Surface reactivity (zone II) is shown when \( \eta < 1 \), indicating low catalyst utilization within the particle. Contour plots of the dimensionless concentration of oxidant inside the particle \( \Theta(r) = C_{\text{ox}}(r)/C_{\text{ox}}^0 \) for each respective case are shown above (colour key: yellow, \( \eta = 1 \); blue, \( \eta = 0 \)).

Now \( v \) is independent of \( C_{\text{ox}}^0 \) and is proportional to \( C_{\text{cat}}^0 \) and the particle volume \( (v \propto R^3) \). Bulk reactivity is reached \( (\eta = 1) \), and the observed rate is controlled by the intrinsic rate of the catalytic reaction \( (k_{\text{cat}}) \). For that reason, kinetic data obtained under these conditions will be most useful for benchmarking.

When diffusion becomes limiting, for large particles or slow diffusion \( \lambda \gg 1 \), again a boundary layer is present near the particle surface. The observed rate is shown in eq 5 (zone IV; Figure 6).

\[ v = \frac{4}{3} N\pi R^3k_{\text{cat}}C_{\text{cat}}^0 \]  

**Figure 6.** Working curve for the observed reaction rate valid for catalyst limited kinetics when \( \mu \leq 10^{-6} \). The vertical axis plots the dimensionless reaction rate \( \tilde{v} = v/(\sqrt{4\pi R D_{\text{ox}} C_{\text{ox}}^0}) \), which varies as a function of \( \lambda = (4R^2k_{\text{cat}}C_{\text{cat}}^0)/(D_{\text{ox}} C_{\text{ox}}^0) \). The vertical dashed-line shows the transition from surface reactivity (zone IV; shaded blue) to bulk reactivity (zone III; shaded red). The dimensionless rate expression for bulk reactivity with catalyst limited kinetics (solid red line; see eq 4) is plotted with the corresponding expression for surface reactivity (solid blue line; see eq 5). Results from the numerical simulations (black dots) are shown for comparison.
Table 1. Diffusing Oxidant: Rate Expressions and Diagnostic Criteria for Limiting Zones

| Zone | Dimensionless Rate $\tilde{\vartheta}$ | Rate $v$ (mol s$^{-1}$) | Orders |
|------|------------------------------------------|-------------------------|--------|
| I    | $\lambda / 3 \mu$                       | $4 \pi R^2 C^{0}_{cat} C^{0}_{ox}$ | 3 1 1 |
| II   | $\lambda / \mu$                         | $2 \pi R^2 C^{0}_{cat} C^{0}_{ox}$ | 3 0 1/2 |
| III  | $\lambda / 3$                           | $2 \pi R^2 C^{0}_{cat} C^{0}_{ox}$ | 2 1 1/2 |
| IV   | $2\sqrt{\lambda} / \mu$                 | $2 \pi R^2 C^{0}_{cat} C^{0}_{ox}$ | 2 1/2 1/2 |

Excellent agreement was found between the approximate analytical expressions for the observed rate in eq 4 (Figure 6, red line) or eq 5 (Figure 6, blue line) and the simulated results (Figure 6, black dots).

**Mixed kinetic control.** A more complex situation arises if we consider $\mu \sim 1$. This is where the rates of the oxidation steps and the rate of the catalytic steps are approximately equal so that neither is predominantly limiting; therefore, the rate expressions will depend on both dimensionless parameters, $\lambda$ and $\mu$. First considering bulk reactivity, which is reached with fast diffusion and/or small particles ($\lambda \ll 1$), the dimensionless rate can be approximated by eq 6.

$$\tilde{\vartheta} = \frac{\lambda}{3(\mu + 1)} + \frac{\mu \lambda^2}{45(\mu + 1)^3}$$

(6)

The validity of this solution can be checked and matches the limiting situations described in the previous sections. When $\mu$ is made either small or large, eq 4 (zone III; catalyst limited kinetics) or eq 2 (zone I; oxidant limited kinetics) are recovered respectively. This is confirmed by numerical simulations shown in Figure S1.

For large particles, when the reaction is confined at or near the surface of the particle ($\lambda \gg 1$), the dimensionless rate becomes

$$\tilde{\vartheta} = 2 \lambda \left(1 - \mu \log \left(\frac{\mu + 1}{\mu}\right)\right)$$

(7)

Similar as above, this solution simplifies to the cases of oxidant limited kinetics described by zone II ($\mu \gg 1$) or catalyst limited kinetics described by zone IV ($\mu \ll 1$). The observed rate predicted by eq 7 matches well with the numerical simulations (Figure S2).

The transition between these behaviours for large particles ($\lambda = 10^5$) upon variation of $\mu$ is shown in Figure 7. It should be noted that when the reaction kinetics become increasingly unsaturated ($k_{cat} C_{ox} \ll k_{cat}$) and the oxidation reaction is rate-determining and very slow ($i.e., \sqrt{\lambda / \mu} < 1$), bulk reactivity is recovered (zone I; Figure 7) and eq 7 is no longer valid. Again, excellent agreement is found between the approximate analytical rate expressions for each limiting zone (Figure 7, solid lines) and the numerical simulations (Figure 7, black dots).

An interesting effect is caused by the depletion of the oxidant over the reaction-diffusion layer when $\lambda > 1$ and $\mu \sim 1$. Nearest to the particle surface the oxidant is present at higher concentrations and the kinetics are saturated $\theta(r) \gg \mu$. Progressing into the particle interior, as the oxidant is depleted over the reaction-diffusion layer, a change to unsaturated kinetics occurs when $\theta(r) \ll \mu$. In effect this means that near the surface, the rate-determining step will reflect the catalytic reaction ($k_{cat}$).

Figure 7. Working curve for the observed reaction rate, valid for large particles and/or slow diffusion ($\lambda = 10^5$). The dimensionless reaction rate $\tilde{\vartheta} = v/(N \pi R D_{ox} C_{ox}^{0})$ is plotted against $\mu = k_{cat}/(k_{cat} C_{ox}^{0})$. The transitions between zones are indicated by the vertical dashed lines. Limiting rate expressions are represented by solid lines: (red line) bulk reactivity/unsaturated (zone I); (green line) surface reactivity/unsaturated (zone II); (blue line) surface reactivity/saturated (zone IV). Results from numerical simulations are shown for comparison (black dots).
Conversely, within the interior of the particle the drop in oxidant concentration causes the oxidation of the catalyst to be rate-determining \((k_{ox})\). As a result, the nature of the rate-determining chemical reaction step will have a spatial dependence within the particle, simply because the concentration of one of the reactants changes significantly as a function of the distance from the surface.

**Oxidant excluded from the MOF pores.**

Next, we turn our attention to diagnosing surface or bulk reactivity when the oxidant is size excluded from diffusing into the pores of the MOF. It would seem that this would trivially always result in surface reactivity; however, considering the redox-activity of many molecular catalysts, it is possible that oxidation of the sites at the particle-solution interface can initiate a diffusional charge hopping processes that carries holes into the interior. In this case, the molecular catalysts inside the particle are responsible for carrying out charge propagation in addition to the catalytic reaction.

To understand this situation in more detail we adopt a simplified mechanism (for WNA) displayed in Figure 8. Here, the catalytic resting state, a nominal Ru\(^{III}\)=O intermediate, is generated by diffusional charge hopping. This intermediate typically reacts with H\(_2\)O in a turnover limiting O-O bond formation step\(^{40,47}\) \((k_1\) in s\(^{-1}\), Figure 8). The substrate (H\(_2\)O), as before, is assumed to maintain a constant concentration. Catalysis proceeds further by a sequence of follow-up reactions (either re-oxidation by charge hopping or purely chemical steps) that are considered to be fast and thus do not appear in the observed rate law. Accounting for the 4e\(^-\) stoichiometry of the OER, the observed rate constant is \(k_{cat} = 4k_1\).

Taking into consideration the heterogeneous interfacial oxidation reaction and diffusional hole hopping inside the MOF particle requires defining two new dimensionless parameters. The first parameter reflects the classical Thiele modulus,

\[
\lambda_e = R \frac{k_{cat}}{D_e}
\]

where \(D_e\) is the apparent diffusion coefficient for charge transport between molecular catalysts within the MOF. The second parameter, \(\gamma\), represents the competition between the heterogeneous reaction involving the oxidant/catalyst and diffusional charge transport:

\[
\gamma = R \frac{k_{ox}^s C_0^{cat}}{C_0^{ox} D_e}
\]

Now, \(k_{ox}^s\) is defined as a second order heterogeneous rate constant \((\text{cm}^2\text{mol}^{-1}\text{s}^{-1})\). Looking at these two control parameters, it is apparent that the reaction-diffusion behaviour of the system will be independent of the catalyst loading \(C_0^{cat}\) when the oxidant is unable to enter the MOF pores. However, the active catalyst concentration \(C_{Ru(V)}\) is a function of distance \(r\) and may be depleted within the particle. Additionally, the solution concentration of oxidant \(C_0^{ox}\) only affects the heterogeneous reaction at the interface (it is not diffusing inside the framework). As shown in the ESI, by taking into account the appropriate boundary conditions, limiting behaviours can be found for large or small values of \(\lambda_e\) and \(\gamma\).

The transition between these reciprocal kinetic regimes (labelled V through VII) is represented in the zone diagram in Figure 9. Rate expressions and diagnostic criteria are summarized in Table 2.

A new case is established when the heterogeneous reaction rate to activate the catalyst, i.e. the hole injection into the particle, is slow compared to the rate of diffusional charge transport (zone V). It follows that \(\gamma \rightarrow 0\), and the observed rate is found to only depend on the interfacial reaction:

\[
\nu = 4\pi R^2 k_{ox}^s C_0^{cat} C_0^{ox}
\]

Catalysis can either take place in the bulk of the particle (zone V(a): small \(\lambda_e\) and \(C_{Ru(V)}(r) = C_0^{cat}\) for all \(r\)) or in a boundary layer at the surface (zone V(b): large \(\lambda_e\)); however, the observed rate is gated by the oxidation of the catalyst at the particle-solution interface. Diagnostics for this situation, both V(a) and V(b), are first order behaviour in both catalyst and oxidant (see Table 2), making this similar to the bulk reactivity case with unsaturated kinetics for a freely diffusing oxidant in the previous section (zone I; eq 2). The discriminating feature is that the rate in eq 10 will depend on the surface area of the particle \((\propto R^2)\) rather than the volume \((\propto R^3)\), and this allows one to assign the heterogeneous oxidation reaction \((k_{ox}^s)\) as rate-determining and that a diffusional charge hopping mechanism is operative.

As mentioned above, \(\lambda_e\) controls the variation between bulk and surface reactivity as diffusional charge transport becomes slower than the catalytic reaction and causes the oxidized form of the catalyst to be confined to a thin layer near the surface.  

---

**Figure 8.** Simplified WNA mechanism (top) where holes \((h^+)\) are supplied to the imbedded molecular catalysts by diffusional charge transport (self-exchange) with an apparent diffusion coefficient \(D_e\). The pores of the MOF are small enough to prevent the external oxidant from entering and diffusing through the particle (bottom). A heterogeneous reaction with rate constant \(k_{ox}^s\) at the particle-solution interface initiates charge propagation.
Table 2. Size Excluded Oxidant (Charge Hopping): Rate Expressions and Diagnostic Criteria for Limiting Zones

| Zone | Dimensionless Rate $\bar{v}$ | Rate $v$ (mol s$^{-1}$) | Orders |
|------|--------------------------------|--------------------------|--------|
| V(a & b) | $\gamma$ | $\frac{4N\pi R^2k_{\text{cat}}^0c_\text{ox}^0}{\lambda_e}$ | 2 1 1 |
| VI | $\frac{4}{3} N\pi R^3k_{\text{cat}}^0c_\text{ox}^0$ | 3 0 1 |
| VII | $\lambda_e$ | $4N\pi R^2C_\text{cat}^0\sqrt{D_e k_{\text{cat}}}$ | 2 0 1 |

Figure 9. Kinetic zone diagram for the case where oxidant is unable to enter particle due to size restrictions. The influence of the heterogeneous oxidation reaction by [ox] at the particle-solution interface is controlled by the dimensionless parameter $\gamma = R(k_{\text{cat}}^0c_\text{ox}^0/D_e)$ on the vertical axis. The horizontal axis plots the classical Thiele modulus for the competition between the catalytic reaction and diffusional charge transport $\lambda_e = R\sqrt{k_{\text{cat}}/D_e}$. Zones displaying bulk reactivity where nearly all the catalyst sites are active are shaded in red. Surface reactivity zones where a boundary layer ensues, which reduces the active catalyst, are shaded in blue. Each limiting zone, where the rate expression does not depend on either dimensionless parameter, is labelled with the corresponding numeral (V to VII; see Table 2 for rate equations). For intermediate cases, where the expression for $\bar{v}$ depends on one or more dimensionless parameters, the controlling parameter(s) are shown in parentheses. The compass in the upper right displays the direction in which increasing a given experimental variable will translate the system within the zone diagram. The boundaries between zones are based on 5% error in the value of the observed steady-state reaction rate ($\bar{v}$).

The expression for the observed rate (as $\gamma \to \infty$) under bulk reactivity (zone VI), and surface reactivity (zone VII), are displayed in eq 11 and eq 12 respectively.

$$v = \frac{4}{3} N\pi R^3k_{\text{cat}}^0c_\text{ox}^0$$ (11)

$$v = 4N\pi R^2C_\text{cat}^0\sqrt{D_e k_{\text{cat}}^{-1}}$$ (12)

When surface reactivity is observed, the reaction-diffusion layer thickness can be defined as $\delta_{\text{rxn}} = \sqrt{D_e k_{\text{cat}}^{-1}}$. In both these cases, since diffusional charge transport carries holes into the MOF particle, the rate is independent of the solution concentration of the oxidant. Furthermore, as expected for conical bulk reactivity in the absence of other limiting factors (oxidation kinetics, diffusion), eq 11 is identical to that for zone III (eq 4) when the oxidant can diffuse through the framework. In these limits, the system only depends on the intrinsic catalytic reaction, which is the ideal operating condition for applications and catalyst benchmarking. Nevertheless, one way to confirm if the oxidant is penetrating and diffusing within the particle or if it is excluded and a charge hopping mechanism is present is to systematically increase the particle size and traverse into a regime where diffusion begins to affect the kinetics (entering either zone IV or zone VII).
Surface vs. bulk reactivity and measured TOFs.

A typical metric used in the kinetic characterization of molecular catalysts incorporated into MOFs is the turnover frequency (TOF). The classical definition of TOF for homogeneous solution phase catalytic reactions is the moles of product generated per unit time divided by the total moles of catalyst present. We have shown here that the possibility of surface reactivity arises due to the coupling of the catalytic reaction to diffusion within the MOF particle, and the active catalytic species are then confined in a reaction layer near the particle surface. Therefore, TOFs obtained taking into account the total amount of catalyst may not reflect the actual activity of the incorporated molecular catalyst. In order to make this distinction more clear, two definitions of TOF need to be adopted,\(^{4,19}\) the apparent turnover frequency (TOF\(_{\text{app}}\)) and the true turnover frequency (TOF\(_{\text{true}}\)):

\[
\text{TOF}_{\text{app}} = \frac{v}{m_{\text{total}}} = \frac{v}{(4/3)\pi R^3 C_{\text{cat}}^0} \quad (13)
\]

\[
\text{TOF}_{\text{true}} = \frac{v}{m_{\text{active}}} = \frac{v}{4\pi R^2 \delta_{\text{rxn}} C_{\text{cat}}^0} \quad (14)
\]

where \(m_{\text{total}} = (4/3)\pi R^3 C_{\text{cat}}^0\) is the total moles of catalyst and \(m_{\text{active}} \sim 4\pi R^2 \delta_{\text{rxn}} C_{\text{cat}}^0\) is the moles of catalyst that effectively participate in the reaction within the reaction layer of thickness \(\delta_{\text{rxn}}\), and \(v\) is the observed reaction rate (production of \(O_2\) in mol s\(^{-1}\)) as defined previously.

The resulting expressions for TOF\(_{\text{app}}\) and TOF\(_{\text{true}}\) are presented in Table 3 for each zone, either bulk or surface reactivity, within the case of a diffusing oxidant as well as that for diffusional charge hopping. Zone V is not displayed because the observed rate is limited by the heterogeneous oxidation reaction at the particle-solution interface rather than the reactions taking place within the interior of the particle. It is readily apparent that when the MOF-catalyst displays surface reactivity due to diffusional limitations on the reaction rate, TOF\(_{\text{app}}\) deviates from an intrinsic kinetic value and is a function of both the particle size (\(R\)) and a particular diffusivity (\(D_{\text{ox}}\) or \(D_e\)). For example, it was found in every case of surface reactivity, TOF\(_{\text{app}}\) will decrease with increasing particle size (TOF\(_{\text{app}} \propto R^{-1}\); zones II, IV, and VII), as an increasing proportion the catalysts are outside \(\delta_{\text{rxn}}\). In some situations where the oxidant freely diffuses through the particle, TOF\(_{\text{app}}\) may also even depend on the catalytic concentration itself (see zones II and IV). These results show that TOF\(_{\text{app}}\) is not ideal for characterizing intrinsic kinetics; however, observing a dependence of TOF\(_{\text{app}}\) on the particle size can be used as a diagnostic for surface reactivity. Conversely, by approximating the size of the reaction layer (\(\delta_{\text{rxn}}\)), which depends on the reaction-diffusion behavior characteristic of each zone, TOF\(_{\text{true}}\) reflects an intrinsic kinetic parameter even under conditions of surface reactivity. Finally, when the experimental variables are optimized and bulk reactivity is obtained, TOF\(_{\text{app}}\) will be independent of the particle size and approximately equal to TOF\(_{\text{true}}\). Under bulk reactivity, both these metrics reflect the kinetic properties of the molecular catalyst inside the MOF pore structure (Table 3; zones III, and VI).

### Table 3. Expressions for TOF\(_{\text{app}}\) and TOF\(_{\text{true}}\) in each limiting kinetic zone

| Zone | TOF\(_{\text{app}}\) (s\(^{-1}\)) | TOF\(_{\text{true}}\) (s\(^{-1}\)) | \(\delta_{\text{rxn}}\) |
|------|-------------------------------|-------------------------------|-----------------|
| I    | \(C_{\text{ox}}^0 k_{\text{ox}}\) | \(k_{\text{cat}} C_{\text{ox}}^0\) | \(\geq R\) |
| II   | \(\frac{3}{2R} C_{\text{ox}}^0 \frac{2D_{\text{ox}} k_{\text{ox}}}{C_{\text{cat}}^0}\) | \(k_{\text{cat}} C_{\text{ox}}^0\) | \(\frac{D_{\text{ox}}}{4K_{\text{ox}}^0 C_{\text{cat}}^0}\) |
| III  | \(k_{\text{cat}}\) | \(k_{\text{cat}}\) | \(\geq R\) |
| IV   | \(\frac{3}{2R} \frac{2D_{\text{ox}} k_{\text{cat}} C_{\text{ox}}^0}{C_{\text{cat}}^0}\) | \(\sim k_{\text{cat}}\) | \(\sim \frac{D_{\text{ox}} C_{\text{ox}}^0}{4K_{\text{cat}}^0 C_{\text{cat}}^0}\) |

Zones of bulk reactivity are shaded red, while surface reactivity zones are shaded blue. Calculation of TOF\(_{\text{true}}\) in zone IV is presented as an estimate, since the reaction layer thickness (\(\delta_{\text{rxn}}\)) is not well-defined due to the non-linear chemical reaction kinetics. The expressions given here are first order approximations as indicated in the table (see ESI for details).

These distinctions in TOF values are particularly important for benchmarking the activity of different MOF-based catalysts. The quantitative analysis presented here demonstrates that the most useful information can be obtained by comparing intrinsic kinetic parameters (TOF\(_{\text{true}}\)) in combination with metrics for catalyst efficiency in terms of bulk versus surface reactivity (e.g., the effectiveness factor, \(\eta\); Figure 5). Furthermore, the microenvironment inside the MOF pore may have a significant influence on the activity of the incorporated molecular catalyst by augmenting its outer coordination sphere. Characterizing this effect may mean comparing the activity of the MOF-embedded species to the homogeneous analogue, where the intrinsic rate of the catalyst (TOF\(_{\text{true}}\)) in each environment, decoupled from mass and charge transport, is of the most value.

### Conclusions

At present, quantitative kinetic studies of MOF-based catalysis are scarce. The interaction of a number of chemical processes including transport phenomena convolute the analysis, and simple predictions as to how the observed rate will respond to changes in reactant concentration, particle size etc. may become non-intuitive. However, as shown here, kinetic evaluation is a necessary step towards the productive utilization MOFs as support matrices for molecular catalysts. Despite having the possibility for a high density of active sites in MOFs, this advantage may be underutilized under certain conditions.

This is primarily because the reaction-diffusion characteristics of the MOF-catalyst construct determine how many of the
imbedded catalysts within the particle participate in the reaction. In this report, taking OER as a target reaction mechanism, we have demonstrated a simple kinetic model to assess and diagnose bulk vs. surface reactivity. It was shown how to transition between these behaviours based on a small number of dimensionless parameters. By modifying certain quantities, for example the particle size, this allows one to take full advantage of the unique material and structural properties of MOFs for highly efficient molecular catalysis. Thus, the quantitative analysis presented here serves as an illustrative example for examining the reaction-diffusion challenge at the heart of MOF-based catalysis and opens the doors for future kinetic studies of catalytic MOFs with a fundamental understanding of the transport phenomena and chemical mechanisms at play.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

Financial support from the European Research Council via Project ERC-CoG2015-6818195, MOFcat is gratefully acknowledged. B.A.I. acknowledges Dr. Vincent C. Wang, Mr. Robin Tyburski, and Dr. Lei Tian for, as always, very stimulating discussions on the matter at hand.

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

Supporting Information

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## Glossary of terms

| Symbol | Meaning | Standard Units |
|--------|---------|----------------|
| $C_i$  | concentration of species $i$ | mol cm$^{-3}$ |
| $C_{\text{cat}}^0$ | total concentration of catalyst or MOF loading | mol cm$^{-3}$ |
| $C_{\text{ox}}^0$ | solution concentration of oxidant | mol cm$^{-3}$ |
| $D_e$  | charge transport diffusion coefficient | cm$^2$ s$^{-1}$ |
| $D_{\text{ox}}$ | intra-MOF diffusion coefficient of freely diffusing oxidant | cm$^2$ s$^{-1}$ |
| $k_{\text{cat}}$ | observed first order catalytic rate constant | s$^{-1}$ |
| $k_d$  | second order rate constant for dimerization in I2M mechanism | cm$^3$ mol$^{-1}$ s$^{-1}$ |
| $k_{\text{ox}}$ | second order rate constant between catalyst and oxidant | cm$^3$ mol$^{-1}$ s$^{-1}$ |
| $k_{\text{s}}$ | second order heterogeneous rate constant between catalyst and oxidant at MOF particle-solution interface | cm$^4$ mol$^{-1}$ s$^{-1}$ |
| $k_1$  | pseudo-first order rate constant for water nucleophilic attack step | s$^{-1}$ |
| $k_2$  | first order rate constant for O$_2$ release step | s$^{-1}$ |
| $K_i$  | kinetic term for coupled chemical reactions of species $i$ | mol cm$^{-3}$ s$^{-1}$ |
| $N$    | total number of MOF particles | n.a. |
| $R$    | MOF particle radius | cm |
| $r$    | radial distance from center of MOF particle | cm |
| $S$    | surface area | cm$^2$ |
| $\text{TOF}^{\text{app}}$ | apparent turnover frequency | s$^{-1}$ |
| $\text{TOF}^{\text{true}}$ | true turnover frequency | s$^{-1}$ |
| $t$    | time | s |
| $\delta_{\text{rxn}}$ | reaction-diffusion layer thickness | cm |
| $v$    | overall observed rate of product (O$_2$) formation | mol s$^{-1}$ |
| $K_i$  | dimensionless kinetic term for coupled chemical reactions of species $i$ | n.a. |
| $\delta$ | dimensionless reaction-diffusion layer thickness $= \delta_{\text{rxn}}/R$ | n.a. |
| $\theta$ | dimensionless concentration of oxidant within MOF particle | n.a. |
| $\tilde{v}$ | dimensionless observed rate of product formation | n.a. |
| $\tilde{i}$ | dimensionless concentration of species $i$ | n.a. |
| $y$    | dimensionless radial distance from center of MOF particle | n.a. |
### Dimensionless Control Parameters

| Symbol | Mechanism/Definition | Statement |
|--------|----------------------|-----------|
| \( \lambda \) | WNA | I2M | catalytic reaction rate / physical diffusion rate of oxidant |
| \( \mu \) | WNA | I2M | catalytic reaction rate / oxidation reaction rate |
| \( \sqrt{\frac{\lambda}{\mu}} \) | WNA | I2M | oxidation reaction rate / physical diffusion rate of oxidant / or / film thickness / reaction-diffusion layer thickness for oxidant |
| \( \kappa \) | I2M | | dimerization reaction rate / \( \text{O}_2 \) release rate |
| \( \lambda_e \) | WNA | | catalytic reaction rate / formal charge transport diffusion rate / or / film thickness / reaction-diffusion layer thickness for charge transport |
| \( \gamma \) | WNA | | interfacial oxidation reaction rate / formal charge transport diffusion rate |
| \( \phi \) | Thiele modulus\(^{S1}\) | | reaction rate / diffusion rate |
Figure S1. Plot of dimensionless reaction rate $\tilde{v} = v/(N\pi R D_{ox} C_{ox}^0)$ as a function of $\mu = k_{cat}/(k_{ox} C_{ox}^0)$ when bulk reactivity is observed ($\lambda = 10^{-3}$), showing the transition from oxidant limited kinetics (zone I, large $\mu$) to catalyst limited kinetics (zone III, small $\mu$). 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 $\mu$ as long as bulk reactivity holds ($\lambda \ll 1$). Vertical dotted line shows the transition between zones.

$$\tilde{v} = \frac{\lambda}{3(\mu + 1)} - \frac{\mu \lambda^2}{45(\mu + 1)^3} \quad \text{eq 6 (main text)}$$
Figure S2. Plot of dimensionless reaction rate $\tilde{v} = v/(N\pi R D_{ox} C_{ox}^0)$ as a function of $\mu = k_{cat}/(k_{ox} C_{ox}^0)$ when surface reactivity is observed ($\lambda = 10^3$), showing the transition from oxidant limited kinetics (zone II, large $\mu$) to catalyst limited kinetics (zone IV, small $\mu$). 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.

\begin{align*}
\text{(--) } \quad \tilde{v} &= \sqrt{2\lambda \left(1 - \mu \ln \left(\frac{\mu + 1}{\mu}\right)\right)} \quad \text{eq 7 (main text)} \\
\text{(--) } \quad \tilde{v} &= \sqrt{\lambda/\mu} \coth \left(\sqrt{\lambda/\mu}\right) - 1 \quad \text{eq S.12}
\end{align*}
A. Freely Diffusing Oxidant within MOF pores

Here we consider the reaction-diffusion problem of a freely diffusing sacrificial oxidant \([\text{ox}]\) (with concentration \(C_{\text{ox}}\)) 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 \([\text{ox}]\) inside the MOF particle is constant and is invariant to changes in concentration (of either \([\text{ox}]\) 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 \([\text{ox}]\) with a second order rate constant, \(k_{\text{ox}}\). A first order rate constant for \(O_2\) 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.

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

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. At steady state, there is a flux of oxidant into the particle, which completely reacts to form the active catalyst. The catalytic reaction is expected to be fast, meaning there is no accumulation of oxidant within the particle. As such the overall rate of product (\(O_2\)) 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, \(D_{\text{ox}}\) is the intra-particle diffusion coefficient of the oxidant, and \(N\) is the total number of particles):

\[
v = NSD_{\text{ox}} \left. \frac{1}{4} \frac{\partial C_{\text{ox}}}{\partial r} \right|_R = N\pi R^2 D_{\text{ox}} \left. \frac{\partial C_{\text{ox}}}{\partial r} \right|_R
\]

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

\[ \begin{align*} 
A + \text{ox} & \overset{k_{\text{ox1}}}{\longrightarrow} B + \text{red} \\
B + \text{ox} & \overset{k_{\text{ox2}}}{\longrightarrow} C + \text{red} \\
C + \text{ox} & \overset{k_{\text{ox3}}}{\longrightarrow} D + \text{red} \\
D + \text{H}_2\text{O} & \overset{k_1}{\rightarrow} E \\
E + \text{ox} & \overset{k_{\text{ox4}}}{\longrightarrow} F + \text{red} \\
F + \text{H}_2\text{O} & \overset{k_2}{\rightarrow} A + \text{O}_2 
\end{align*} \]

Given that water is the solvent as well as the substrate, the concentration of \text{H}_2\text{O} is taken as constant throughout the particle, which gives the pseudo-first order rate constant \(k_1\). The reaction-diffusion equations become

\[ \begin{align*} 
\frac{\partial \text{C}_{\text{ox}}}{\partial t} &= D_{\text{Ce}} \left( \frac{\partial^2 \text{C}_{\text{ox}}}{\partial r^2} + \frac{2}{r} \frac{\partial \text{C}_{\text{ox}}}{\partial r} \right) - k_{\text{ox1}} \text{C}_{\text{ox}} \text{C}_A - k_{\text{ox2}} \text{C}_{\text{ox}} \text{C}_B - k_{\text{ox3}} \text{C}_{\text{ox}} \text{C}_C - k_{\text{ox4}} \text{C}_{\text{ox}} \text{C}_E \\
\frac{\partial \text{C}_A}{\partial t} &= -k_{\text{ox1}} \text{C}_{\text{ox}} \text{C}_A + k_2 \text{C}_F \\
\frac{\partial \text{C}_B}{\partial t} &= k_{\text{ox1}} \text{C}_{\text{ox}} \text{C}_A - k_{\text{ox2}} \text{C}_{\text{ox}} \text{C}_B \\
\frac{\partial \text{C}_C}{\partial t} &= k_{\text{ox2}} \text{C}_{\text{ox}} \text{C}_B - k_{\text{ox3}} \text{C}_{\text{ox}} \text{C}_C \\
\frac{\partial \text{C}_D}{\partial t} &= k_{\text{ox3}} \text{C}_{\text{ox}} \text{C}_C - k_1 \text{C}_D \\
\frac{\partial \text{C}_E}{\partial t} &= k_1 \text{C}_D - k_{\text{ox4}} \text{C}_{\text{ox}} \text{C}_E \\
\frac{\partial \text{C}_F}{\partial t} &= k_{\text{ox4}} \text{C}_{\text{ox}} \text{C}_E - k_2 \text{C}_F 
\end{align*} \]

With the initial and boundary conditions as follows

**t = 0, \ \forall r:** \( \text{C}_{\text{ox}} = \text{C}^0_{\text{ox}}, \ \text{C}_B = 0, \ \text{C}_C = 0, \ \text{C}_D = 0, \ \text{C}_E = 0, \ \text{C}_F = 0, \ \text{C}_A = \text{C}\text{\textsubscript{cat}}^0 \)

**t > 0, \ r = 0:** \( \frac{\partial \text{C}_{\text{ox}}}{\partial r} = 0 \)

**t > 0, \ r = R:** \( \text{C}_{\text{ox}} = \text{C}^0_{\text{ox}}, \ \frac{\partial \text{C}_A}{\partial r} = 0, \ \frac{\partial \text{C}_B}{\partial r} = 0, \ \frac{\partial \text{C}_C}{\partial r} = 0, \ \frac{\partial \text{C}_D}{\partial r} = 0, \ \frac{\partial \text{C}_E}{\partial r} = 0, \ \frac{\partial \text{C}_F}{\partial r} = 0 \)

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

\[ \text{C}_A + \text{C}_B + \text{C}_C + \text{C}_D + \text{C}_E + \text{C}_F = \text{C}^0_{\text{cat}} \]  

(S.1)

Application of steady-state yields
\[ D_{\text{ox}} \left( \frac{\partial^2 C_{\text{ox}}}{\partial r^2} + \frac{2 \partial C_{\text{ox}}}{r \partial r} \right) = k_{\text{ox}1} C_{\text{ox}} C_A + k_{\text{ox}2} C_{\text{ox}} C_B + k_{\text{ox}3} C_{\text{ox}} C_C + k_{\text{ox}4} C_{\text{ox}} C_E \]  
\[ k_{\text{ox}1} C_{\text{ox}} C_A = k_2 C_F \]
\[ k_{\text{ox}2} C_{\text{ox}} C_B = k_{\text{ox}1} C_{\text{ox}} C_A \]
\[ k_{\text{ox}3} C_{\text{ox}} C_C = k_{\text{ox}2} C_{\text{ox}} C_B \]
\[ k_1 C_D = k_{\text{ox}3} C_{\text{ox}} C_C \]
\[ k_{\text{ox}4} C_{\text{ox}} C_E = k_1 C_D \]
\[ k_2 C_F = k_{\text{ox}4} C_{\text{ox}} C_E \]

Solving this system of equations for \( K_{\text{ox}} = k_{\text{ox}1} C_{\text{ox}} C_A + k_{\text{ox}2} C_{\text{ox}} C_B + k_{\text{ox}3} C_{\text{ox}} C_C + k_{\text{ox}4} C_{\text{ox}} C_E \) using eq S.1 gives

\[ K_{\text{ox}} = \frac{4 C_{\text{ox}} C_{\text{cat}}}{k_2 + \frac{C_{\text{ox}}}{k_1} + \frac{1}{k_{\text{ox}1}} + \frac{1}{k_{\text{ox}2}} + \frac{1}{k_{\text{ox}3}} + \frac{1}{k_{\text{ox}4}}} \]  
\[ \text{(S.3)} \]

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

\[ \frac{1}{k_{\text{ox}}} = \frac{1}{k_{\text{ox}1}} + \frac{1}{k_{\text{ox}2}} + \frac{1}{k_{\text{ox}3}} + \frac{1}{k_{\text{ox}4}} \]  
\[ \text{(S.4)} \]

Substitution into eq S.2 yields

\[ D_{\text{ox}} \left( \frac{\partial^2 C_{\text{ox}}}{\partial r^2} + \frac{2 \partial C_{\text{ox}}}{r \partial r} \right) = \frac{4 k_{\text{ox}} C_{\text{ox}} C_{\text{cat}}}{k_2 + k_{\text{ox}} C_{\text{ox}} + 1} \]  
\[ \text{(S.5)} \]

Dimensional analysis by defining \( \theta = \frac{C_{\text{ox}}}{C_{\text{ox}}^0}, \) \( \bar{r} = \frac{r}{R} \), results in two dimensionless control parameters:

\[ \mu = \frac{k_{\text{cat}}}{k_{\text{ox}} C_{\text{ox}}^0}, \quad \lambda = R^2 \frac{4 k_{\text{cat}} C_{\text{cat}}^0}{D_{\text{ox}} C_{\text{ox}}^0} \]

where,

\[ k_{\text{cat}} = \frac{k_1 k_2}{k_1 + k_2} \]  
\[ \text{(S.6)} \]

After rearrangement,

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

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

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

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = R^2 \frac{4 k_1 k_2}{c_{\text{ox}}^0} \left[ \frac{1}{d_{\text{ox}} \left( k_1 + k_2 \right)} \theta + \frac{k_1 k_2}{k_{\text{ox}} c_{\text{ox}}^0 (k_1 + k_2)} \right]
\]

the equation to be solved becomes

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

with the dimensionless reaction rate given by

\[
\tilde{v} = \frac{v}{N \pi R D_{\text{ox}} c_{\text{ox}}^0} = \left. \frac{\partial \theta}{\partial y} \right|_1
\] (S.8)

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

\[
K_{\theta} = \frac{\lambda \theta}{\mu + \theta}
\] (S.9)

which essentially reflects Michaelis-Menten type kinetics for the overall reaction as described in the main text. Reference models52,53 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 \( \theta \) can only take values between zero and one, if \( \mu \gg 1 \) then eq S.7 further reduces to

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = \lambda \frac{\theta}{\mu}
\] (S.10)

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

\[
\phi^2 = \frac{\lambda}{\mu} = R^2 \frac{4 k_{\text{ox}} C_{\text{cat}}^0}{D_{\text{ox}}}
\]

Integration of (S.10) taking into account the appropriate boundary conditions54 yields the dimensionless concentration profile:

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

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

\[
\tilde{v} = \frac{\sqrt{\frac{\lambda}{\mu}} \cosh \left( \sqrt{\frac{\lambda}{\mu}} \right) - \sinh \left( \sqrt{\frac{\lambda}{\mu}} \right)}{\sinh \left( \sqrt{\frac{\lambda}{\mu}} \right)}
\] (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 film.

\[ \tilde{v} = \frac{\lambda}{3\mu} \quad \text{(zone I)} \]

(S.13)

**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.

\[ \tilde{v} = \sqrt{\lambda/\mu} \quad \text{(zone II)} \]

(S.14)

**Internal Effectiveness factor \( \eta \) for oxidant limited kinetics**

Since this limiting behavior matches the Thiele model\(^{51}\) for many reaction-diffusion systems in porous particles, an expression for the effectiveness factor \( \eta \) can be obtained.\(^{54}\) 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.

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

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

A plot of \( \eta \) 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 problem\(^{55}\) 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 film (\( \theta \sim 1 \)). For the moment, \( \mu \) can take any value (large or small). Since \( \lambda \) is very small we can consider it a regular perturbation and write an asymptotic expansion given by \( \theta = \theta_0 + \lambda \theta_1 + \lambda^2 \theta_2 + \ldots \).\(^{56}\) Then, rewriting eq S.7 as
\[ \nabla^2 \theta = \frac{\lambda}{\mu + \theta} \]  

(S.16)

\( O(1) \) 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

\[ \nabla^2 \lambda \theta_1 + \nabla^2 \lambda^2 \theta_2 + \cdots = \frac{\lambda}{\mu + 1 + \lambda \theta_1 + \lambda^2 \theta_2 + \cdots} \]

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

\[ \nabla^2 \lambda \theta_1 + \nabla^2 \lambda^2 \theta_2 + \cdots = \left( \frac{\lambda}{\mu + 1} \right) \left( \frac{1 + \lambda \theta_1 + \lambda^2 \theta_2 + \cdots}{1 + \lambda \theta_1 + \frac{\lambda^2 \theta_2 + \cdots}{\mu + 1}} \right) \]

\[ = \left( \frac{\lambda}{\mu + 1} \right) \left( 1 - \frac{\lambda \theta_1 + \cdots}{\mu + 1} \right) (1 + \lambda \theta_1 + \cdots) \]

\[ = \frac{\lambda}{\mu + 1} + \frac{\mu \lambda^2}{(\mu + 1)^2} \theta_1 + \cdots \]

\( O(\lambda) \) terms:

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

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

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

\[ y^2 \frac{\partial \theta_1}{\partial y} = \frac{1}{3 \mu + 1} y^3 + C_1, \frac{\partial \theta_1}{\partial y} \bigg|_0 = 0; C_1 = 0; \frac{\partial \theta_1}{\partial y} = \frac{1}{3 \mu + 1} \]

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

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

\( O(\lambda^2) \) terms:

\[ \frac{1}{y^2} \frac{\partial}{\partial y} \left( y^2 \frac{\partial \theta_2}{\partial y} \right) = \frac{\mu}{(\mu + 1)^2} \theta_1 \]

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

\[ \int \partial \left( y^2 \frac{\partial \theta_2}{\partial y} \right) = \int \frac{\mu y^2 (y^2 - 1)}{6(\mu + 1)^3} \partial y \]
\[ y^2 \frac{\partial \theta_2}{\partial y} = \left( \frac{\mu}{6(\mu+1)^3} \right) \left( \frac{y^5}{5} - \frac{y^3}{3} + C_3 \right); \quad \frac{\partial \theta_2}{\partial y} \bigg|_0 = 0; \quad C_3 = 0 \]

\[ \frac{\partial \theta_2}{\partial y} = \left( \frac{\mu}{6(\mu+1)^3} \right) \left( \frac{y^3}{5} - \frac{y}{3} \right) \]

\[ \int \frac{\partial \theta_2}{\partial y} = \int \left( \frac{\mu}{6(\mu+1)^3} \right) \left( \frac{y^3}{5} - \frac{y}{3} \right) \, dy \]

\[ \theta_2 = \frac{\mu(3y^4 - 10y^2 + C_4)}{360(\mu+1)^3}; \quad \theta_2(1) = 0; \quad C_4 = 7; \quad \theta_2 = \frac{\mu(3y^4 - 10y^2 + 7)}{360(\mu+1)^3} \]

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 system still depends on two dimensionless parameters (both \( \lambda \) and \( \mu \)); however, two 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:

\[ \tilde{v} = \frac{\lambda}{3} \]  

(zone III)  

(S.19)

**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

\[ \tilde{v} = \frac{\lambda}{3\mu} \]  

(zone I)  

(S.20)

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

A derivation to a similar problem\(^{55}\) 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 $\theta$, the overall reaction could switch from zeroth order kinetics with respect to oxidant near the particle surface (where $\theta \to 1$) to first order kinetics near the interior of the particle (where $\theta \to 0$). 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 $\delta_{rxn}$ 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 $\theta$ and $\mu$, the right hand side is $O(1)$, and consequently,

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

The boundary layer thickness is therefore,

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

Then it is possible to rescale the radial coordinate to $\delta$.\(^{57}\)

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

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

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

with the boundary conditions: $z = 0: Y = 1$; and $z \geq \delta: Y \to 0$

Where now the solution for the inner region can be sought in the form of a regular asymptotic expansion\(^{56}\) given by,

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

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

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

$$\frac{\partial Y_0}{\partial z} \left( \frac{\partial^2 Y_0}{\partial z^2} \right) = \frac{\partial Y_0}{\partial z} \left( \frac{Y_0}{\mu + Y_0} \right)$$

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

S13
\[
\left(\frac{\partial Y_0}{\partial z}\right)^2 = Y_0 + C_1 - \mu [\ln(\mu + Y_0) + C_2]; \frac{\partial Y_0}{\partial z} \to 0 \text{ as } Y_0 \to 0, \text{ so } C_1 = 0, \text{ and } C_2 = -\ln \mu
\]

\[
\frac{\partial Y_0}{\partial z} = -\sqrt{2 \left( Y_0 - \mu \ln \left( \frac{\mu + Y_0}{\mu} \right) \right)}
\]

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

\[
\sqrt{\varepsilon} \frac{\partial \theta}{\partial y} \sim \sqrt{2 \left( \theta - \mu \ln \left( \frac{\mu + \theta}{\mu} \right) \right)}
\]

\[
= \sqrt{2\lambda \left( \theta - \mu \ln \left( \frac{\mu + \theta}{\mu} \right) \right)}
\]

\[
\theta(1) = 1, \text{ therefore}
\]

\[
\left. \frac{\partial \theta}{\partial y} \right|_1 = \sqrt{2\lambda \left( 1 - \mu \ln \left( \frac{\mu + 1}{\mu} \right) \right)} + O(\sqrt{\varepsilon})
\]

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 = \( O(\sqrt{\varepsilon}) \),

\[
\tilde{\nu} = \sqrt{2\lambda \left( 1 - \mu \ln \left( \frac{\mu + 1}{\mu} \right) \right)}
\]

(S.24)

\((\text{zone IV and IV})\)

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

\[
\tilde{\nu} = \sqrt{2\lambda}
\]

(S.25)

\((\text{zone IV})\)

**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

\[
\tilde{\nu} = \sqrt{\frac{\lambda}{\mu}}
\]

(S.26)

\((\text{zone II})\)

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

**Reaction-diffusion layer (boundary layer) analysis (\( \delta = \delta_{\text{rxn}}/R \))**

**Zone II**
With \( \mu \gg 1 \), eq S7 can be written as

\[
\nabla^2 \theta = \frac{\lambda}{\mu} \theta
\]

When \( \lambda/\mu \) 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,

\[
\delta_{\text{rxn}} = \left( \frac{D_{\text{ox}}}{4k_{\text{ox}}C_{\text{cat}}^0} \right)^{1/2}
\]  \( \text{(S.27)} \)

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 \( \delta \),\(^{57}\)

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

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\(^{56}\) given by, \( Y = Y_0 + \sqrt{\varepsilon}Y_1 + \varepsilon Y_2 + ... \)

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,

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

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 ($\theta = \frac{C_{ox}(r)}{C_{ox}^0}$ 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,

$$\delta_{rxn} \sim \sqrt{\frac{D_{ox}C_{ox}^0}{4k_{cat}C_{cat}^0}}$$  \hspace{1cm} (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, $\frac{\partial Y_0}{\partial z} \bigg|_0 = -\sqrt{2}$. Integration with these boundary conditions results in

$$Y_0 = \frac{z^2}{2} - \sqrt{2}z + 1$$  \hspace{1cm} (S.30)
\( O(\sqrt{\varepsilon}) \) terms:

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

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 \( \approx 1 \). 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, \( \frac{\partial Y_1}{\partial z} \bigg|_0 = 0 \) and \( Y_1(0) = 0 \), the result is

\[
Y_1 = \frac{z^3}{3} - \frac{\sqrt{2}}{2}z^2
\]

(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 \( (1 - \delta) < y < 1 \)):

\[
\theta = \lambda \left( 1 - \frac{1}{3} \right) + \left( \frac{\lambda}{2} - \frac{\sqrt{2} \lambda}{2} \right) (1 - y)^2 - \sqrt{2} \lambda (1 - y) + 1
\]

(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 \( \theta \to 0 \) and \( \theta \ll \mu \). As can be seen from the simulated results in Figure S4, \( \theta \) rapidly approaches zero outside the boundary layer and as \( y \to 0 \). This condition is not met with eq S.32, which clearly is not equal to zero as \( y \to 0 \) (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 \( \delta_{rxn} \) 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 $\theta$ approaches zero.
A.2 Formal Reaction-Diffusion Kinetic Model for I2M Mechanism

\[ A + ox \xrightarrow{k_{ox1} \text{(fast)}} B + \text{red} \]
\[ B + ox \xrightarrow{k_{ox2}} C + \text{red} \]
\[ C + ox \xrightarrow{k_{ox3}} D + \text{red} \]
\[ 2D \xrightarrow{k_d} E \]
\[ E + 2H_2O \xrightarrow{k_2} 2B + O_2 \]

Given that water is the solvent as well as the substrate, the concentration of H\(_2\)O is taken as constant throughout the particle. The reaction-diffusion equations become

\[
\frac{\partial C_{ox}}{\partial t} = D_{ox} \left( \frac{\partial^2 C_{ox}}{\partial r^2} + \frac{2 \partial C_{ox}}{r \partial r} \right) - k_{ox1} C_{ox} C_A - k_{ox2} C_{ox} C_B - k_{ox3} C_{ox} C_C \\
\frac{\partial C_A}{\partial t} = -k_{ox3} C_{ox} C_A \\
\frac{\partial C_B}{\partial t} = k_{ox1} C_{ox} C_A - k_{ox2} C_{ox} C_B + 2k_2 C_E \\
\frac{\partial C_C}{\partial t} = k_{ox2} C_{ox} C_B - k_{ox3} C_{ox} C_C \\
\frac{\partial C_D}{\partial t} = k_{ox3} C_{ox} C_C - 2k_d C_D^2 \\
\frac{\partial C_E}{\partial t} = k_d C_D^2 - k_2 C_E 
\]

With the initial and boundary conditions as follows

\[ t = 0, \ \forall r: C_{ox} = C_{ox0}, \ C_B = 0, \ C_C = 0, \ C_D = 0, \ C_E = 0, \ C_A = C_{cat}^0 \]
\[ t > 0, \ r = 0: \frac{\partial C_{ox}}{\partial r} = 0 \]
\[ t > 0, \ r = R: C_{ox} = C_{ox0}, \ \frac{\partial C_A}{\partial r} = 0, \ \frac{\partial C_B}{\partial r} = 0, \ \frac{\partial C_C}{\partial r} = 0, \ \frac{\partial C_D}{\partial r} = 0, \ \frac{\partial C_E}{\partial r} = 0 \]

At the particle-solution interface (\( r = R \)), forced convection from stirring maintains a constant concentration of [ox], \( C_{ox}(t, R) = C_{ox0}^0 \). Mass balance on the catalytic intermediates gives \( \forall t \) and \( \forall r \),

\[ C_A + C_B + C_C + C_D + C_E = C_{cat}^0 \]  \hspace{1cm} (S.33)

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

\[
D_{ox} \left( \frac{\partial^2 C_{ox}}{\partial r^2} + \frac{2 \partial C_{ox}}{r \partial r} \right) = k_{ox1} C_{ox} C_B + k_{ox3} C_{ox} C_C \\
2k_2 C_E = k_{ox2} C_{ox} C_B \\
k_{ox2} C_{ox} C_B = k_{ox3} C_{ox} C_C 
\]
\[ k_{\text{ox}3} C_{\text{ox}} C_C = 2 k_d C_D^2 \]

\[ k_d C_D^2 = k_2 C_E \]

\[ C_B = \frac{2 k_d C_D^2}{k_{\text{ox}2} C_{\text{ox}}} \]

\[ C_C = \frac{2 k_d C_D^2}{k_{\text{ox}3} C_{\text{ox}}} \]

\[ C_E = \frac{k_d C_D^2}{k_2} \]

Substitution into eq S.33 gives

\[
\frac{2 k_d C_D^2}{k_{\text{ox}2} C_{\text{ox}}} + \frac{2 k_d C_D^2}{k_{\text{ox}3} C_{\text{ox}}} + \frac{k_d C_D^2}{k_2} + C_D - C^0_{\text{cat}} = 0
\]

\[
\left( \frac{2 k_d}{k_{\text{ox}2} C_{\text{ox}}} + \frac{2 k_d}{k_{\text{ox}3} C_{\text{ox}}} + \frac{k_d}{k_2} \right) C_D^2 + C_D - C^0_{\text{cat}} = 0
\]

\[
\frac{k_d}{k_2} \left[ \frac{2 k_2 (k_{\text{ox}2} + 1) + C_{\text{ox}}}{C_{\text{ox}}} \right] C_D^2 + C_D - C^0_{\text{cat}} = 0 \quad (S.35)
\]

Substitution into (S.34), we can write

\[
D_{\text{ox}} \left( \frac{\partial^2 C_{\text{ox}}}{\partial r^2} + \frac{2 \partial C_{\text{ox}}}{r \partial r} \right) = 4 k_d C_D^2 \quad (S.36)
\]

Dimensional analysis by defining \( \theta = \frac{C_{\text{Ce}}}{C_{\text{ox}}} \), \( \tilde{i} = \frac{i}{C_{\text{cat}}} \), \( y = \frac{r}{R} \), results in four dimensionless control parameters:

\[
\kappa = \frac{4 k_d C^0_{\text{cat}}}{k_2}, \quad \mu = \frac{2 k_2}{k_{\text{ox}3} C_{\text{ox}}}, \quad \lambda = R^2 \frac{4 k_2 C^0_{\text{cat}}}{D_{\text{ox}} C_{\text{ox}}}, \quad \rho = \frac{k_{\text{ox}3}}{k_{\text{ox}2}}
\]

Eq S.30 can be rewritten as

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = \frac{\kappa \lambda}{4} \bar{D}^2 \quad (S.37)
\]

Additionally, (S.35) becomes

\[
\frac{k_d}{k_2} \left[ \frac{2 k_2}{k_{\text{ox}3} C_{\text{ox}}} \left( \frac{k_{\text{ox}3}}{k_{\text{ox}2}} + 1 \right) + \theta \right] \bar{D}^2 + \bar{D} - 1 = \left[ \frac{\kappa}{4} \left( \frac{\mu (\rho + 1) + \theta}{\theta} \right) \right] \bar{D}^2 + \bar{D} - 1 = 0
\]

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

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = \frac{\lambda}{\kappa} \left( \frac{1 + \kappa \left( \frac{\mu (\rho + 1) + \theta}{\theta} \right) - 1}{\left( \frac{\mu (\rho + 1) + \theta}{\theta} \right)^2} \right)^2 \quad (S.38)
\]

with the dimensionless reaction rate given by
\[ \dot{\nu} = \frac{v}{N \pi R D_{ox} C_{ox}^0} = \frac{\partial \theta}{\partial y} \bigg|_1 \]  

(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 \( k_{ax2} \gg k_{ax3} \) so that \( \rho \rightarrow 0 \). This simplification gives,

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = \frac{\lambda}{\kappa} \left( \frac{1 + \kappa \left( \frac{\mu + \theta}{\theta} \right) - 1}{\left( \frac{\mu + \theta}{\theta} \right)^2} \right) 
\]

(S.40)

which is now a function of only three dimensionless parameters.

\[
\kappa = \frac{4 k_d C_{cat}^0}{k_2}, \quad \mu = \frac{2 k_2}{k_{ox3} C_{ox}^0}, \quad \lambda = R^2 \frac{4 k_2 C_{cat}^0}{D_{ox} C_{ox}^0} 
\]

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

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = \frac{\lambda}{\mu + \theta} 
\]

(S.41)

We can now define \( K_{\theta} \) given below

\[
K_{\theta} = \frac{\lambda}{\mu + \theta} 
\]

(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 \( \kappa \), and therefore, are the same as in the WNA mechanism for each limiting kinetic behavior; however, the definitions of the dimensionless control parameters \( \lambda \) and \( \mu \), 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

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2 \partial \theta}{y \partial y} = \frac{\lambda \theta}{\mu + \theta} 
\]

(S.43)

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

\[
\phi^2 = \frac{\lambda}{\mu} = R^2 \frac{2 k_{ox3} C_{cat}^0}{D_{ox}} 
\]
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), $\sqrt{\lambda/\mu} \ll 1$:**

$$\tilde{v} = \frac{\lambda}{3\mu}$$

(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 system still depends on two dimensionless parameters (both $\lambda$ and $\mu$); however, two limits can be defined.

**Bulk reactivity ($O_2$ release limited kinetics), $\mu \ll 1$:**

$$\tilde{v} = \frac{\lambda}{3}$$

(S.48)

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

$$\tilde{v} = \frac{\lambda}{3\mu}$$

(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 $\theta$, the overall reaction could switch from zeroth order kinetics with respect to oxidant near the particle surface (where $\theta \to 1$) to first order kinetics near the interior of the particle (where $\theta \to 0$). 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
\[
\tilde{\nu} = \sqrt{2\lambda \left(1 - \mu \ln\left(\frac{\mu + 1}{\mu}\right)\right)} \tag{S.50}
\]

**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.

\[
\tilde{\nu} = \sqrt{\frac{\lambda}{\mu}} \tag{S.51}
\]

**Surface reactivity (\(O_2\) release limited kinetics), \(\mu \ll 1\):**

When \(\mu \ll 1\), the \(O_2\) release step is rate-determining, and the expression in S.50 simplifies to

\[
\tilde{\nu} = \sqrt{2\lambda} \tag{S.52}
\]

**I2M-2: fast \(O_2\) release (\(\kappa \to 0\))**

When \(\kappa\) is much smaller than unity, this implies the oxygen release step is faster than the dimerization step. Then, depending on the magnitude of \(\lambda\) and \(\mu\) several subcases are described below.

**Subcase I2M-2A: oxidant limited kinetics (\(\mu \kappa \gg 1\))**

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).

\[
\tilde{\nu} = \sqrt{\frac{\lambda}{\mu}} \coth\left(\sqrt{\frac{\lambda}{\mu}}\right) - 1 \tag{S.53}
\]

**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

\[
\frac{\partial^2 \theta}{\partial y^2} + \frac{2}{y} \frac{\partial \theta}{\partial y} = \frac{\lambda \kappa}{4} \tag{S.54}
\]

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

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

\[
\theta = \frac{\lambda \kappa}{24} (y^2 - 1) + 1 \tag{S.55}
\]

\[
\tilde{\nu} = \frac{\lambda \kappa}{12} \tag{S.56}
\]

\[
\nu = \frac{4}{3} N \pi R^3 k_d (C_{cat}^0)^2
\]
This result shows that the observed rate \( (v) \) in eq S.56 is second order in \( C_{\text{cat}}^0 \), 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 \( C_{\text{ox}}^0 \).

**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 \( \kappa \) and \( \lambda \).
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.\textsuperscript{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 ($k_{\text{cat}} = 4k_1$). Water is the solvent and substrate, and its concentration is assumed constant as above. The generalized reaction scheme is given below.

\[
A|_{r=R} + \text{ox}|_{r=R} \xrightarrow{k_{3e}^{\text{ox}}} B|_{r=R} + \text{red}|_{r=R}
\]

\[
(D_e) \quad B + A \rightleftharpoons A + B
\]

\[
B + H_2O \xrightarrow{k_{\text{cat}}} A + O_2
\]

The governing equations and boundary conditions are

\[
\frac{\partial C_B}{\partial r} \bigg|_{r=0} = 0 \quad \frac{\partial C_A}{\partial r} \bigg|_{r=0} = 0
\]

\[
0 < r < R \quad \frac{\partial C_B}{\partial t} = D_e \left( \frac{\partial^2 C_B}{\partial r^2} + \frac{2}{r} \frac{\partial C_B}{\partial r} \right) - k_{\text{cat}} C_B
\]

\[
\frac{\partial C_A}{\partial t} = D_e \left( \frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) + k_{\text{cat}} C_B
\]

\[
C_A + C_B = C_{\text{cat}}^0
\]

\[
C_{\text{ox}} = 0
\]

\[
r = R
\]

\[
\frac{\partial C_B}{\partial t} \bigg|_{r=R} = -D_e \frac{\partial C_B}{\partial r} \bigg|_{r=R} + k_{3e}^{\text{ox}} C_{\text{ox}} C_A^r = R
\]

\[
r > R
\]

\[
C_{\text{ox}} = C_{\text{ox}}^0
\]

\[
C_A = 0, \quad C_B = 0
\]
Application of steady state to eq S.57 and eq S.58, focusing our attention on intermediate B, yields

\[ D_e \left( \frac{\partial^2 C_B}{\partial r^2} + \frac{2}{r} \frac{\partial C_B}{\partial r} \right) = k_{cat} C_B \]  \hspace{1cm} (S.59)

\[ D_e \frac{\partial C_B}{\partial r} \bigg|_{r=R} = k_{ox}^s C_0^0 C_{A}^R \]  \hspace{1cm} (S.60)

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

\[ v = NSD_e \frac{\partial C_B}{\partial r} \bigg|_{r=R} = 4N\pi R^2 D_e \frac{\partial C_B}{\partial r} \bigg|_{r=R} \]  \hspace{1cm} (S.61)

Dimensional analysis by defining \( i = \frac{C_i}{c_{cat}} \), \( y = \frac{r}{R} \), results in two dimensionless control parameters:

\[ \lambda_e = R \sqrt{\frac{k_{cat}}{D_e}} \]

\[ \gamma = R \frac{k_{ox}^s C_0^0}{D_e} \]

The equations to solve become:

\[ \frac{\partial^2 \tilde{B}}{\partial y^2} + \frac{2}{y} \frac{\partial \tilde{B}}{\partial y} = \lambda_e^2 \tilde{B} \]  \hspace{1cm} (S.62)

\[ \frac{\partial \tilde{B}}{\partial y} \bigg|_1 = \gamma \tilde{B}^{y=1} \]  \hspace{1cm} (S.63)

with the dimensionless rate,

\[ \tilde{v} = \frac{\partial \tilde{B}}{\partial y} \bigg|_1 = \frac{v}{4N\pi R D_e c_{cat}^0} \]  \hspace{1cm} (S.64)

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

\[ \frac{\partial \tilde{B}}{\partial y} \bigg|_1 = B^{y=1}(\lambda_e \coth \lambda_e - 1) \]  \hspace{1cm} (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:

\[ \tilde{v} = \frac{\partial \tilde{B}}{\partial y} \bigg|_1 = \gamma(1 - B^{y=1}) \]

\[ B^{y=1} = 1 - \frac{\tilde{v}}{\gamma} \]

Plugging this result into eq S.65 and solving for \( \tilde{v} \) yields the dimensionless expression for the rate.
\[
\tilde{\nu} = \frac{\lambda_e \coth \lambda_e - 1}{1 + \frac{\lambda_e \coth \lambda_e - 1}{\gamma}}
\]

(S.66)

\[
\frac{1}{\tilde{\nu}} = \frac{1}{\gamma} + \frac{1}{\lambda_e \coth \lambda_e - 1}
\]

Four limiting situations are straightforwardly obtained for large or small values of \(\lambda_e\) and \(\gamma\). These are displayed in the zone diagram in Figure 7 of the main text.

**Bulk reactivity \(\lambda_e \to 0\):**

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

\[
\frac{\lambda_e^2}{\gamma} \to \infty
\]

\[
\tilde{\nu} = \gamma
\]

zone \(V(a)\)  
(S.67)

\[
\frac{\lambda_e^2}{\gamma} \to 0
\]

\[
\tilde{\nu} = \frac{\lambda_e^2}{3}
\]

zone \(VI\)  
(S.68)

**Surface reactivity \(\lambda_e \to \infty\):**

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

\[
\frac{\lambda_e}{\gamma} \to \infty
\]

\[
\tilde{\nu} = \gamma
\]

zone \(V(b)\)  
(S.69)

\[
\frac{\lambda_e}{\gamma} \to 0
\]

\[
\tilde{\nu} = \lambda_e
\]

zone \(VII\)  
(S.70)

**Reaction-diffusion layer (boundary layer) thickness \(\delta = \delta_{\text{rxn}} / R\):**

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

\[
\nabla^2 \tilde{B} = \lambda_e^2 \tilde{B}
\]

The balance of dominant terms gives

\[
\frac{\tilde{B}}{(\delta)^2} \sim \lambda_e^2 \tilde{B}
\]
\[ \delta = \frac{1}{\lambda_e} \]

\[ \delta_{\text{rxn}} = \sqrt{\frac{D_e}{k_{\text{cat}}}} \]  

(S.71)

The boundary layer analysis for zone \textbf{VII} is identical to the situation in zone \textbf{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 \( \lambda_e \gg 1 \) and \( \frac{\lambda_e}{\gamma} \ll 1 \).
C. MOF Structural Parameters

\( m_{\text{cat}} \) = average number of catalyst sites per pore  
\( n_{\text{cat}} \) = total moles of catalyst used in catalytic assay (mol)  
\( V_{\text{pore}} \) = average pore volume (cm\(^3\))  
\( V_{\text{cat}} = V_{\text{pore}} / m_{\text{cat}} \) = average volume of pore per catalyst (cm\(^3\))  
\( N_A = 6.02 \times 10^{23} \) (mol\(^{-1}\))  
\( V_{\text{MOF}} \) = MOF particle volume (= \( 4/3\pi R^3 \)) (cm\(^3\))  
\( N \) = total number of MOF particles used in the catalytic assay

Calculation of \( \nu \) requires \( N \) and \( C_{\text{cat}}^0 \), which are given by

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

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 non-linear 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 (\( \Delta y \)) of 0.001.\(^{510}\) The flux of oxidant at the particle surface (\( y = 1 \)) was computed using an asymmetric three-point discretization,\(^{510}\) also second order (error = \( O(\Delta y^2) \)). A method of successive substitution\(^{511}\) (or “relaxation method”\(^{512}\)) was used to approximate the unknown non-linear term (\( K_\theta \)) 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 non-linear 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 \( \leq 10^{-5} \)).
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