Wavelet-based surrogate time series for multiscale simulation of heterogeneous catalysis¹

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Abstract We propose a wavelet-based scheme that encodes the essential dynamics of discrete microscale surface reactions in a form that can be coupled with continuum macroscale flow simulations with high computational efficiency. This makes it possible to simulate the dynamic behavior of reactor-scale heterogeneous catalysis without requiring detailed concurrent simulations at both the surface and continuum scales using different models. Our scheme is based on the application of wavelet-based surrogate time series that encodes the essential temporal and/or spatial fine-scale dynamics at the catalyst surface. The encoded dynamics are then used to generate statistically equivalent, randomized surrogate time series, which can be linked to the continuum scale simulation. We illustrate an application of this approach using two different kinetic Monte Carlo simulations with different characteristic behaviors typical for heterogeneous chemical reactions.

Keywords: Wavelet based transformation; Random surrogates; Kinetic Monte Carlo; Temporal upscaling; Multiscale modeling of catalysis

1. Introduction and Background

Accounting for dynamic, multiscale, spatiotemporal interactions is a major concern in computational simulation of chemical reactions (Mishra et al., 2008a). This is especially true for heterogeneous catalysis (Saliccioli et al., 2011; Stamatakis, 2015), where molecular and mesoscale chemical reactions at the catalyst surface must ultimately be linked to continuum-scale hydrodynamic processes in a fluid phase. This is especially important when the rate controlling processes involved at either or both scales are significantly nonlinear and thus sensitive to the effects of external inputs. However, such inter-scale coupling poses major challenges that are frequently beyond current computational capabilities. Thus, we are motivated to seek approaches that can reduce the need for running detailed concurrent simulations at all the scales, while still preserving the important dynamics associated with

scale-to-scale interactions. Specifically, we are concerned with simulating the basic reaction system summarized in Fig. 1. The key features of this system include: 1) a fluid that contains both reactant and product species moving past a solid catalytic surface (the coarsest scale); 2) interphase transport between the fluid and solid surface; 3) adsorption/desorption of reactant and product molecules onto catalytic sites on the surface; and 4) reactions at the surface on the catalytic sites (the finest scale). For the fluid phase, we assume that the dynamics can be simulated with a continuum model, such as those used for computational fluid dynamics (CFD). For the surface, we assume that the dynamics should be simulated with a model that accounts for discrete physics, such as molecular dynamics or kinetic Monte Carlo (kMC) to account for molecular-scale and surface topological effects such as facet specific selectivity, etc. The main issue then becomes how to accurately account for the dynamical interactions between these two types of models across these widely different spatiotemporal scales. We expect this to be especially relevant to situations where the goal is to design catalysts with surface properties that improve expected global reaction performance (e.g., higher conversion, improved selectivity, lower operating temperature, improved durability).

Previous approaches (Maestri and Cuoci, 2013; Matera et al., 2014) have been proposed for coupling the multiple scales involved in heterogeneous catalysis, i.e. to transfer the micro scale catalytic surface reaction kinetics information to the continuum (macro scale) fluid flow field. Matera et al. (Matera et al., 2014) propose an efficient and stable method to integrate first-principles based kMC (1p-kMC) reaction microkinetics into computational fluid dynamics (CFD) by interpolating irregularly gridded 1p-kMC data using time-averages of approximate kMC steady-state reaction rates as source terms for the CFD conservation equations. The use of time averages would appear to exclude the detailed dynamic effects of short-time-scale concentration/rate fluctuations on the macro-scale behavior, but this issue does not appear to have been resolved as yet. One possible workaround to the time averaging

issue may be to implement on-the-fly kMC simulations or pre-computed kMC simulations at selected intervals. However, such methods may be inefficient when millions to billions of kMC cases are needed to account for the non-uniform dynamic evolution of the system. Thus, to account more accurately for the dynamic consequences of the small-scale perturbations on the macro-scale dynamics, it is necessary to construct an efficient concurrent coupling strategy that is both suitable for large-scale CFD simulations and yet still upwardly communicates the essential dynamic information generated at the micro-scale to the larger system.

Figure 1 Illustration of the basic reaction system of interest. The fluid phase behaves according to continuum hydrodynamics (orange lines) with relatively large spatial (e.g., $>10^{-3}$ m) and temporal (e.g., $>10^{-3}$ s) scales. Reactant (green arrows) and product (red arrows) molecules transport between the fluid and surface phases. Surface reactions occurring on discrete catalytic sites can span ranges that include much smaller spatial and temporal scales (e.g., $<10^{-6}$ m and $<10^{-6}$ s).

Other methods proposed for reducing the micro-scale computational burden in multi-scale simulations are reviewed by (Vvedensky, 2004). Some publications (Bi and Li, 2004; Dollet, 2004; Mishra et al., 2008b) specifically address reaction and surface problems related

to the problem of interest here. Two widely utilized approaches for addressing the multiscale problem are the so-called gap tooth (Kevrekidis et al., 2002) and time stepping (Kevrekidis et al., 2002; Vasenkov et al., 2006) methods. Wavelet-based methods have also received much attention for addressing both spatial (Frantziskonis and Deymier, 2000; Frantziskonis, 2002a, 2002b; Frantziskonis et al., 2006; Mishra et al., 2008a) and temporal scaling (Frantziskonis and Deymier, 2003; Frantziskonis et al., 2006). In particular, one recent review paper (Hariharan and Kannan, 2014) describes the application of wavelet-based methods for simulating reaction-diffusion systems and cites almost 140 relevant publications. Other wavelet-based scaling methodologies include the dynamic compound wavelet matrix technique of Muralidharan et al. (Muralidharan et al., 2008) and the time-parallel compound wavelet matrix technique of Frantziskonis et al. (Frantziskonis et al., 2009). Other wavelet applications to reaction-diffusion simulations are those by Bindal et al. (Bindal et al., 2003), Stundzia and Lumsden (Stundzia and Lumsden, 1996), Burger and Ruiz-Baier (Burger and Ruiz-Baier, 2009), Chen et al. (Chen et al., 2010), Ewing et al. (Ewing et al., 2004), Hariharan and Kannan (Hariharan and Kannan, 2010a, 2010b, 2009), and Cai and Zhang (Cai and Zhang, 1998).

Wavelet-based techniques offer certain advantages over other multiscale methods because they provide scale-wise data fusion mechanisms that allow ready upscaling and downscaling of dynamic features (Frantziskonis et al., 2006). In addition, wavelet transformation has the advantage that it preserves non-stationary features in the dynamics that would be lost or significantly distorted by other types of infinite basis transforms (e.g., Fourier analysis). This becomes more important when the information generated by fine-scale models is limited in extent and includes non-stationary effects.

On the other hand, like Fourier transforms, it is possible to use wavelet transforms to generate ‘surrogate’ data series; that is, artificial data series that are equivalent dynamical

replicates (but still individually unique), which retain the same key statistical and dynamical properties as the original data. Surrogate data methods have been widely used for several years in characterizing and testing null hypotheses with data from complex dynamical systems (Breakspear et al., 2003; Keylock, 2006; Rouyer et al., 2008), but our use of surrogates here is directed towards a different problem: the transfer of dynamic information across scales. Specifically, in this study we are concerned with the need to minimize the need for long time-scale simulations of the fine-scale dynamics that would consume large amounts of computational resources. Expressed in another way, we desire to use the results from relatively short simulations of the fine-scale dynamics to generate longer or wider equivalent data sequences that can be coupled with coarse-scale simulations. To minimize artifacts, our objective is to create surrogates that retain the most important dynamical features in the fine-scale data that could have significant impacts on the coarse scale by carrying moments (mean, variance, etc.) of the final scale statistics. The surrogates then can serve as substitutes for fine-scale information to ‘fill in the gaps’ between updated fine-scale simulations.

In the following sections, we describe our proposed surrogate generation methodology and illustrate its application to a simulated problem in heterogeneous catalysis where the surface reaction rates are modeled with a multistep kMC model. We then describe how we expect surrogates of this type can be used as a general “upscaling interface” to transfer the important dynamical information from the fine scale to the coarse scale.

2. Proposed approach for generating surrogates

As noted above, we propose a wavelet-based approach for encoding the fine-scale dynamic information from the catalyst surface because wavelet transforms provide a natural framework for consolidating information associated with multiple length and time scales. Since the theory and motivation for wavelet analysis are already widely covered in the literature, we do not repeat those details here, but we refer the reader to the following major

references on the subject (Frantziskonis et al., 2009, 2006; Mishra et al., 2008a, 2008b). Our focus here is rather on proposing how one might adapt the wavelet transform methodology to upscale dynamic information from fine scales at the catalyst surface to coarse scales in the fluid (represented as spatial and temporal computational discretization scales typical for CFD).

As illustrated in Fig. 2, we are concerned with translating the impact of dynamic fluctuations at the surface to computational grid points associated with continuum simulations of the fluid. For example, we obtain concentrations $\{D\}_d$ in the fluid domain arising from surface reactions at sites R (e.g., modeled with kMC). Here, d represents the data resolution required for the CFD simulation. The wavelet transform of $\{R\}_r$, where r is the resolution of the surface dynamics yields $W_R(s, t)$, i.e. a set of wavelet coefficients, where s represents scale and t stands for time. Now, $W_R(s, t)$ can be decomposed as

$$W_R(s, t) = f_R(s_0, \Delta t) \oplus f_R(s_1, \Delta t) \oplus f_R(s_2, 2^1 \Delta t) \oplus \dots \oplus f_R(s_n, 2^{n-1} \Delta t) \quad (1)$$

i.e. into $n = \log_2(r) - 2^2$ number of scales. Here, $\oplus$ represents the scale-wise association in the wavelet analysis formalism, Δt denotes the time step in the surface simulation, $f_R(s_i, 2^{i-1} \Delta t)$, $i = 1, 2, \dots, n$ represents the wavelet transform at scale s_i with the scaling interval $2^{i-1} \Delta t$ and $f_R(s_0, \Delta t)$ represents the wavelet transform at the coarsest scale for a particular scaling function.

Figure 2 Schematic of the proposed approach for upscaling fine-scale surface dynamics to CFD simulation in the fluid phase. Here, ‘R’ denotes a catalytic reaction site and ‘D’ a node in the diffusive-convective computational grid.

At this point, we focus on time upscaling to simplify the details, although the method can also be equally applied to spatial upscaling. To connect the disparate time scales between the catalyst surface and the fluid, we use the procedure described below to extend the wavelet coefficients of the fine-scale reaction dynamics to generate ‘surrogate’ representations of the dynamic concentration vector that reflect dynamics occurring at time scales commensurate to the CFD simulation. Thus, we obtain the concentration vector $\{D\}_d$ needed to link the dynamic surface chemistry to the CFD simulation. A stepwise description of this process is summarized in Table 1. A relevant and detailed flow chart is provided in Fig. S1 of the supplementary material.

Table 1 Proposed algorithm for wavelet-based surrogate generation

Step-1: Choose two or more consecutive fine-scale data sets (of the same length) with converged statistics. Convergence is examined through the variance of increments or “variogram” $\gamma(r)$, a function of the time lag, r , defined as (Frantziskonis, 2002a, 2002b)
$$2\gamma(r) = \sum_{i=1}^N \{x(i) - x(i+r)\}^2 / N$$
 with x denoting the value of the data at position i , for N total number of points. The variogram is used to estimate the maximum autocorrelation distance and spacing in time needed to reach statistical stationarity.

Step-2: Apply the discrete wavelet transform (DWT) to all the fine-scale data sets.

Step-3: Use the wavelet coefficients from each of the data set to identify the cutoff scale (point of separation) between fine and coarse dynamic domains. The cutoff scale is usually identified based on the fraction of the total variance (power) associated each scale (e.g., the scale at which the fraction of the variance associated with still larger scales drops below a cutoff value, such as 10%).

Step-4: Apply a linear weighting of the coarse scales from all the data sets to obtain an estimate of coarse scale wavelet coefficients for predicting longer time scale behavior.

<p><u>Step-5:</u> For each fine scale in the data sets, obtain a linear weighted average of the wavelet coefficients at each scale and then estimate the statistical distributions of the entire population of fine-scale wavelet coefficients.</p>	<p><u>Step-6:</u> Generate random numbers with distributions corresponding to the fine-scale wavelet coefficient distributions from step 5.</p>
<p><u>Step-7:</u> Carry out a similar process as mentioned above for generating random but statistically equivalent realizations of wavelet coefficients for the longer time scale surface dynamics.</p>	<p><u>Step-8:</u> Combine the randomly generate wavelet coefficients from both the coarse and fine scales and use the inverse wavelet transformation to obtain the upscaled surrogate data, which can be coupled with CFD.</p>

We note that the accuracy of the above technique increases with the number of data sets used for a given system, but the algorithm is described, for the sake of simplicity, with respect to two data sets for a given system. For data where the coarse scale response is relatively simple, two data sets suffice. It is also worth noting that the computational efficiency depends on the problem addressed, and in particular on how quickly the particular data converge statistically. It is assumed that the computational efficiency is similar to other methods such as gap-tooth. However, our proposed method offers computationally efficient upscaling since it only requires operations of order N where N is the number of data points.

3. Example applications

To illustrate the application of the above algorithm, we apply it to two different examples of surface catalytic reactions modeled with lattice kMC simulation. The software package we

used is called KMOS (Hoffmann et al., 2014), which uses the variable step size method for kMC. As kMC is a widely used and published method for modeling the dynamics of heterogeneous catalytic reactions, we do not include an extensive background review of that here and instead recommend the following references regarding details of the method (Gillespie, 1977; Hoffmann et al., 2014; Jansen, 2012; Núñez and Vlachos, 2015; Schaefer and Jansen, 2013).

3.1 Example 1: CO adsorption equilibrium on Pd (100)

For our first example problem, we consider the simple case of CO adsorption on Pd (100) under steady state conditions. For this simulation, we consider only one distinct surface site and one gaseous species, CO. Only two possible reaction steps can occur: CO adsorption and CO desorption. In this case, three dynamic steady states are possible, depending on the rates for adsorption and desorption. If the adsorption rate is high and the desorption rate is low, the surface will become covered very quickly and remain so on average. If the adsorption rate is low and the desorption rate constant is high, the surface coverage will stabilize at a low average level. Finally, if the rates are close in magnitude, the coverage will reach a steady state with a medium average coverage. In all three cases, the statistical nature of the kMC dynamics results in microscale fluctuations of the net global surface coverage and gas phase CO concentration as CO molecules adsorb and desorb at individual sites over time. It is the effects of these fluctuations that we seek to dynamically upscale using wavelets. The surface concentration is expressed in a normalized coverage (0 to 1) based on a lattice-saturated monolayer (Savara et al., 2009) and is commonly called “ θ ” in the surface science literature.

For the current example, we specify the process transition rates for adsorption and desorption for this model as follows

$$k_{ads} = \frac{S_0 P^* A_g}{\sqrt{2\pi k_B T M}} \quad (2)$$

$$k_{des} = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where P denotes the input pressure of the gas (typically in Pa), A_g is the size of the geometric area of an individual molecular adsorption site (typically in m^2), S_0 is dimensionless and is analogous to the steric factor in reactive hard spheres collision theory, k_B is the Boltzmann constant (with units of J K^{-1}), T the temperature in K, and M the mass of an individual molecule (typically in kg), respectively. In this simplified model, the adsorption rate includes gas fluxes based on kinetic theory. The desorption rate constant follows an Arrhenius relationship, where, A denotes an Arrhenius pre-exponential factor (typically units of s^{-1}) which is free from concentration units, R is the ideal gas constant, E_a is the activation energy for process (in Joules per mol), and the exponential term describes the statistical likelihood for a desorption event to occur.

In the present example we assumed a temperature of 600 K and a sample size of 400 unit cells, corresponding to a surface with dimensions of 70x70 Angstroms. Under these conditions, the adsorption rate and desorption rate are balanced such that at steady state, a medium surface coverage will exist. The values used for the pre-exponentials and activation energies can be found in Table A1 in the appendix, and are based on experimental data (Behm et al., 1980).

3.2 Example 2: Methanol adsorption on CeO_2 (111)

For our second example problem, we consider a kMC simulation of the simplified chemical reaction network summarized in Table 2. In this network, an initial input flux of methanol gas interacts with a defect free CeO_2 (111) surface, which has three distinct sites:

Ce, O, and an intermediate bridge site for methanol adsorption processes. The kMC model then simulates the results of having the surface continuously exposed to methanol at a pressure of 1 bar, although the gas phase is not truly present in the kMC simulation; the pressure simply serves as a parameter for the adsorption rate constant. As methanol is the only input gas, the first step is methanol adsorption. In this model, the transition rates for adsorption processes can include an activation energy and are defined as

$$k_{ads} = \frac{S_0 P^* A_g}{\sqrt{2\pi k_B T M}} \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where the variables are as described above. The first term represents the input flux of the gas and serves as the pre-exponential for the Arrhenius form and the exponential term represents the statistical likelihood for adsorption, based on the activation energy for adsorption at a given temperature.

Following methanol adsorption, additional steps involving desorption, association and ionic dissociation occur in the following sequence (numbers indicate sequential reactions):

Formaldehyde Production: 3 → 5 → 6 → 7

Methanol Production: 3 → 4

H₂ Production: 3 → 5 → 2 → 1

This reaction sequence results in output fluxes of methanol, H₂ and formaldehyde. The transition rates for desorption, associative and dissociative processes all take the form

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where the variables are defined as above. The pre-exponentials and activation energies used in the simulation can be found in Table A1 in the appendix.

Table 2 Reaction processes within the sample reaction network

Reaction Number	Reaction Name	Chemical Equation
1	H ₂ production	$2(\text{H}^* \text{-- Ce}^{4+} \text{-- O}^{2-}) \rightarrow$ $\text{H}_2(\text{g}) + 2 \text{Ce}^{4+} \text{-- O}^{2-}$
2	H* production	$\text{Ce}^{3+} \text{-- O}^{2-} \text{-- H}^+ \rightarrow$ $\text{H}^* \text{-- Ce}^{4+} \text{-- O}^{2-}$
3	Methanol Adsorption	$\text{CH}_3\text{OH}(\text{g}) + 2 \text{Ce}^{4+} \text{-- O}^{2-} \rightarrow$ $\text{Ce}^{4+} \text{-- O}^{2-} \text{-- CH}_3\text{OH} \text{-- Ce}^{4+} \text{-- O}^{2-}$
4	Methanol Desorption	$\text{Ce}^{4+} \text{-- O}^{2-} \text{-- CH}_3\text{OH} \text{-- Ce}^{4+} \text{-- O}^{2-} \rightarrow$ $\text{CH}_3\text{OH}(\text{g}) + 2 \text{Ce}^{4+} \text{-- O}^{2-}$
5	Ionic Methoxy Production	$\text{Ce}^{4+} \text{-- O}^{2-} \text{-- CH}_3\text{OH} \text{-- Ce}^{4+} \text{-- O}^{2-} \rightarrow \text{CH}_3\text{O}^- \text{-- Ce}^{4+} \text{-- O}^{2-}$ $+ \text{Ce}^{4+} \text{-- O}^{2-} \text{-- H}^+$
6	H abstraction from Ionic Methoxy	$\text{CH}_3\text{O}^- \text{-- Ce}^{4+} \text{-- O}^{2-} + 2 \text{Ce}^{4+} \text{-- O}^{2-} \rightarrow$ $\text{CH}_2\text{O} \text{-- Ce}^{4+} \text{-- O}^{2-} + \text{Ce}^{3+} \text{-- O}^{2-} + \text{H}^* \text{-- Ce}^{4+} \text{-- O}^{2-}$
7	Formaldehyde Desorption	$\text{CH}_2\text{O} \text{-- Ce}^{4+} \text{-- O}^{2-} \rightarrow$ $\text{CH}_2\text{O}(\text{g}) + \text{Ce}^{4+} \text{-- O}^{2-}$

The reaction network has been tested at a temperature of 600 K and the activation energies and pre-exponential factors have been selected based on existing density functional theory and experimental literature (Savara, 2015). The simulation size consists of 100 unit cells, corresponding to a surface with dimensions of 38.25×66.26 Angstroms. The kMC simulations were run until a steady-state rate of production was reached, and snapshots have been output every 10000 steps and steady state was reached after approximately 100 snapshots. The corresponding output fluxes for each gaseous species (i.e., production rates

from desorption process) was converted to units of molecules/m²/s and utilized for temporal upscaling.

4. Results and discussion

4.1 Example-1

For the CO adsorption/desorption case, the predicted temporal variation of surface CO concentration is depicted in Figure 3a (this surface concentration is in units of relative coverage, which is normalized to 1). The kMC simulation covers a total physical time of 56.1 μ s, which amounts to 16384 temporal points with a variable time step. The simulated data points were evenly mapped into the time domain by linear interpolation, resulting in an average time step $\Delta t = 0.0035 \mu$ s. Statistical analysis of the resulting time series reveals that it has a significant degree of autocorrelation and appears to have the general characteristics of colored noise (Hanggi and Jung, 1995).

To characterize the fine-scale dynamics, the kMC time series were then separated into four sequential data sets each of 4096 points. Variograms of these data sets (depicted in Figs. 3b and 3c) reveal that the variance of the original time series fluctuates considerably over short periods of time, but there is also a longer time scale autocorrelation period of roughly 200 temporal points. Considering these temporal characteristics, we chose a sample length of 4096 points for generating the initial wavelet transforms. Various statistical measures, shown in Fig. S2 (a)-(d) of the supplementary material, demonstrate the convergence with respect to the number of data points and the stability of the proposed algorithm. Based on this statistical information and on the variograms, the prediction of CO concentration data is based herein on cycles of 4096 data points.

Figure 3 (a) CO concentration time series generated by the kMC adsorption/desorption model. (b) Variograms γ for each of four subsets of the CO time series. (c) Average variogram for the entire CO time series with zoom-in at the first 1000 points in the inset.

Figure 4a depicts a scalogram (density plot of the wavelet transform coefficients in a time versus scale space) of the CO concentration time series, and Fig. 4b shows the normalized energy of the wavelet transform coefficients with respect to scale for the four data sets used in Fig. 3. Scale 1 corresponds to the coarsest scale while scale 12 is the finest available scale. It can be seen that the energy is concentrated at coarse scales, which reflects the longer-time-scale autocorrelation in the data. The concentration of energy at coarse scales is important to include in representing the scale-wise energy of the wavelet coefficients.

Figure 4 (a) A typical scalogram of CO concentration. (b) Normalized energy of wavelet transform coefficients with respect to scale. Energy concentration spots are within the circle.

Using the algorithm described above, surrogates of the original CO time series were generated as depicted in Fig. 5 (a1)-(c1). As previously explained, wavelet coefficients for the fine scales (above the cutoff scale) were generated based on the fine scale component, while the coarse-scale behavior (below the cutoff scale) was generated through the weighted averaging process described. Comparisons of the surrogates with the original CO time series in both time and wavelet space reveal what appears to be good agreement. Comparison of the first, second, third, and fourth statistical moments also indicate good agreement as shown in Fig. S3 (a)-(d) of the supplementary material. To examine the stability and convergence of the model, scale-specific energies of the predicted and provided data are compared in Fig. 5 (a2)-(c2), where the close agreement is seen. It can be concluded that the proposed surrogate generation method is sufficiently capable in providing stable and converged data sets.

Figure 5 Comparison of surrogate data segments with the original kMC CO time series (a1) between data-1 and data-2; (b1) between data-2 and data-3 and (c1) between data-3 and data-4. Original CO data are shown in blue and predicted in red. Normalized energy of wavelet transform coefficients are shown on the right-hand side: (a2) between data-1 and data-2; (b2) between data-2 and data-3 and (c2) between data-3 and data-4.

4.2 Example-2

Figure 6 illustrates the reaction rate time series and corresponding variograms for the three different gases (methanol, formaldehyde and hydrogen) generated by the kMC

simulation of the reaction network in Table 2. A total physical time of 56.1 μs was run by kMC, resulting in 8192 temporal points with variable time step. As before, the time series were evenly mapped to the total time space by linear interpolation with a $\Delta t = 0.0035 \mu\text{s}$. Compared with the first example time series, these time series appear to be much closer to uncorrelated white noise. These characteristic results in wavelet coefficients with most of the energy concentrated at finer (short) time scales. To simplify comparisons with the first example, we also chose data segments of length 4096 points for making the initial wavelet transforms. Different statistical measures are shown in Fig. S4 (a)-(d) of the supplementary material.

Figure 6 Time series and corresponding variograms γ for the generation rates of methanol, formaldehyde and hydrogen generated by the second kMC reaction network simulation.

The scalograms and normalized component coefficient energies resulting from the wavelet transforms of each reaction rate time series are displayed in Fig. 7. It can be seen that most of the energy is concentrated at fine scales, increasing their relevance in multi-scale dynamic predictions.

Figure 7 Scalograms and normalized coefficients of the transformed reaction rate time series from the second example kMC reaction simulation. Areas of high energy concentration are noted within the circle.

Using the above algorithm, statistically and dynamically equivalent surrogates of the original time series and their corresponding transforms were generated as depicted in Fig. 8. Fig. 8 (a1)-(c1) shows the scale-wise predicted “randomly realized surrogates” of the provided methanol (CH_3OH), formaldehyde (CH_2O) and (c) hydrogen (H_2) reaction rate dates. The predicted data is validated by comparing the scale-specific energy of the predicted

data to that of the provided data. Figure 8 (a2)-(c2) shows very good agreement between provided and predicted data. Various statistical measures, shown in Fig. S5 (a)-(d) of the supplementary material, demonstrate the convergence with respect to the number of data points and the stability of the proposed algorithm. Here, between two data sets of 4096 points each, eight data sets each having 4096 data points are predicted. For each predicted data set the scale-specific energy is close to the range of the scale-specific energy for the provided data sets.

Figure 8 Comparisons of the surrogate and original kMC-generated reaction rate time series for methanol, formaldehyde, hydrogen. Blue colors indicate segments of the original data

used to generate the surrogate time series (in red). Comparisons of the corresponding normalized wavelet component energies are on the right.

4.3 Upscaling the surface reaction dynamics from examples 1 and 2

As explained above, our intended goal is to generate surrogates that contain essential information about the surface reaction dynamics that can be transferred to longer time scales relevant to the fluid phase. To illustrate the results of this process for the example problems, we applied the scale-limited inverse wavelet transformation to the wavelet transforms generated from the 4096 time step data segments to generate surrogates spanning much longer times. Figures 9a,b compare the kMC-generated and upscaled surrogate CO time series over a long time interval consisting of 32768 time steps. Figure 9(c) depicts the wavelet transform coefficient energies for these same time series. We note that in the upscaling process, the scale limited inverse wavelet transform utilizes only the 7 coarsest scales, and thus the upscaling expands the original kMC information by 8 dyadic scales. While the specific details in each time series are clearly different, they are statistically and dynamically equivalent.

Figure 9 Comparison of the entire original kMC simulated CO time series (a) with an upscaled surrogate (b). Normalized wavelet component energies of CO time series and its surrogate.

Figure 10 Comparison of the entire original kMC simulated reaction rate time series (a1-a3) with upscaled surrogates (b1-b3). Normalized wavelet component energies for each time series and its surrogate (c1-c3).

Similar results from upscaling of the reaction rate time series from example 2 are illustrated in Fig. 10. As before, both the original time series and surrogate are random samples of an infinite set of realizations of the underlying dynamics, so their details are different but their statistics and dynamic modes are virtually identical, as revealed by the normalized wavelet component energies in 10 (c1-c3). In this case, the coarse-scale surrogate features result from the 10 coarsest wavelet scales, thus the upscaling here spans 5 dyadic scales.

5. Conclusions and prospect

From the example results presented here, it appears that the proposed algorithm, consisting of wavelet transforms and sampling statistically equivalent realizations, can be used to generate wavelet-based surrogate time series of steady-state surface catalytic reactions generated by fine-scale discrete models that can be translated to scales relevant to continuum fluid phase models. We find that the algorithm is unconditionally stable and it is possible to generate statistically and dynamically equivalent surrogate time series for long times based from segments of much shorter, model-generated time series. The resulting surrogates appear to do a good job of replicating both short-time-scale stochastic features as well as longer time scale correlations associated with complex surface reactions. Thus, we expect that it should be possible to use these surrogates to reduce the computational overhead required to make combined simulations of the multi-scale interactions that can occur in heterogeneous catalytic systems.

Although this study shows the generation of surrogates based on stochastic microscale data, the proposed method should be applicable to deterministic microscale problems. The same process would hold provided the deterministic process converges in a way similar to the statistical one.

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Appendix

Table A1 Pre-exponential factors and activation energies used for each kMC simulated sample reaction network

Process name	Pre-exponential (s^{-1})	Activation Energy (J/mol)
CO Adsorption Equilibrium on Pd (100)		
CO adsorption	8.83×10^4	0
CO desorption	2×10^{16}	153971
Methanol Adsorption on CeO_2 (111)		
H_2 production	10^{13}	110000
H^* production	10^{15}	230000
Methanol Adsorption	4.82×10^7	0
Methanol Desorption	10^{13}	110125
Ionic Methoxy Production	10^{10}	107986
H abstraction from Ionic Methoxy	10^{10}	40000
Formaldehyde Desorption	10^{13}	91000