

Small Number of Active Sites and Single-Locus Kinetics Revealed in (salph)Co-Catalyzed Ethylene Oxide Polymerization

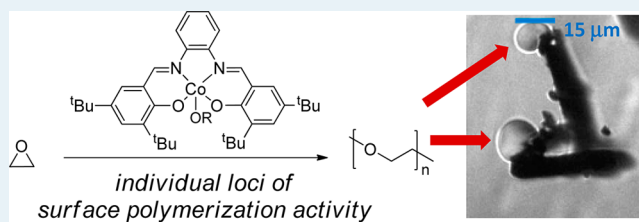
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Supporting Information

ABSTRACT: The single-particle resolution of in operando bright-field optical microscopy revealed that only a small fraction of (salph)Co crystals showed high initial catalytic activity with EO. In addition, each active particle displayed individual loci of reactivity rather than uniform reactivity distributed over the entire particle. Growth kinetics at an individual locus showed stepwise periods of higher and lower activity. This reactivity distribution data and single-locus kinetics data would not be available through a traditional ensemble technique that examined bulk material properties.

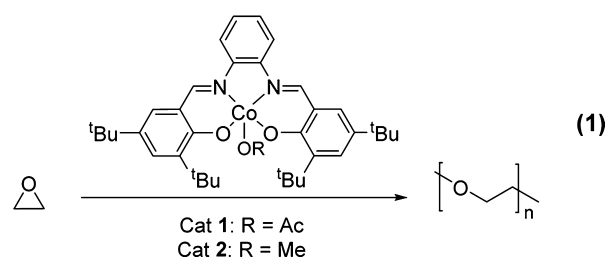
KEYWORDS: heterogeneous catalysis, microscopy, polymerization, single-particle, single-crystal, kinetics, epoxide, bright-field imaging



In heterogeneous catalysis, the number of active sites per particle often determines the efficiency and selectivity of the reaction, yet the determination of the number of catalytically active sites per particle remains a significant challenge.¹ Complicating this measurement, within the same batch of catalyst some particles may exhibit multiple individual active sites while others have none.^{1–3} Furthermore, individual active sites might cycle between states with higher or lower activity, the characterization of which is not possible through the rate averaging inherent to bulk-materials measurements.

Building on the earlier work of Weckhuysen,^{4–8} Domke,⁹ Hofkens,^{10–12} Chen,^{13,14} and our group¹⁵ with in operando IR, nonlinear Raman, and fluorescence microscopy to image catalysts under catalytic conditions, we now report that bright-field optical microscopy characterizes the distribution of catalyst activity in cobalt-catalyzed ethylene oxide polymerization. To the best of our knowledge, this represents the first in operando optical microscopy study with single-crystal resolution of metal-catalyzed epoxide polymerization, an important process for industrial¹⁶ and small-scale synthesis.¹⁷

Coates recently disclosed (salph^{tBu})CoOAc **1** and (salph^{tBu})CoOMe **2** as the most highly isotactic catalysts reported to date for *rac*-propylene oxide (PO) polymerization.¹⁸ These catalysts were proposed to be heterogeneous, with polymerization of the epoxide occurring at the interface of liquid monomer and the surface of crystals of **1** and **2**.¹⁹ To understand the origin of this stereoselectivity, it would assist to know if the reactivity and thus stereoselectivity is coming from a small number of active sites or from broad surface reactivity. We therefore turned to in operando bright-field optical microscopy imaging of ethylene oxide (EO) polymerization—relevant for materials synthesis in its own right^{20–22}—catalyzed by **1** and **2** (eq 1); Gaseous EO was selected as the monomer to prevent the dissolution of the polymer that complicated analysis with liquid PO.



These studies reveal a small number of active sites per particle. Furthermore, only a small fraction of all particles of **1** showed high ethylene oxide polymerization activity (Figure 1). The variation in catalytic activity of different particles of **1** might be accounted for by a small number of initial active sites

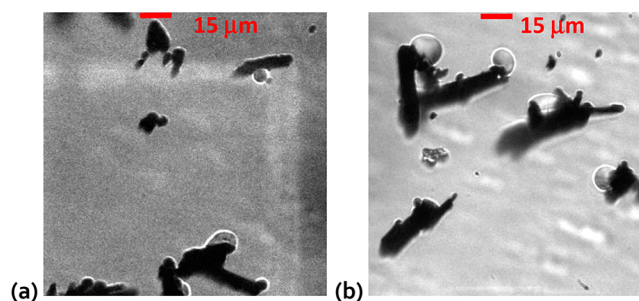


Figure 1. Representative microscopy images ($136 \times 136 \mu\text{m}^2$) showing single beads of clear PEO from individual active sites or localized clusters of active sites on dark **1**. (a) After 4 h. PEO present on less than 10% of all particles. Shape indicates “bursts” from a small number of initial active sites; (b) After 14 h. Single-loci (or localized groups of sites) of reactivity, present on less than 20% of all particles.

Received: August 3, 2013

Published: August 7, 2013

on each crystal. This information would not be available through a bulk material assay that provided averaged ensemble properties of the sample.

Evidence supporting individual activity “bursts” also was detected on smaller crystals as individual beads of clear polymer on the dark surface of **1** (Figure 2). Importantly, control

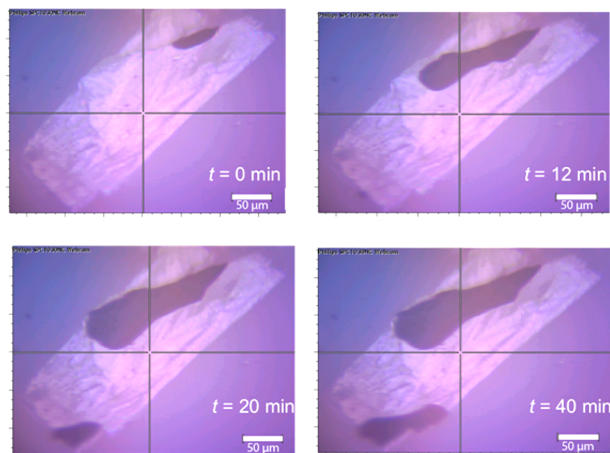
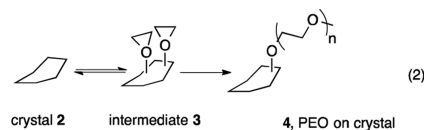


Figure 2. Representative microscopy images ($417 \times 308 \mu\text{m}^2$) showing initiation and expanding areas of dark growth at two locations on a crystal of catalyst **2**.

reactions monitoring **1** in the absence of EO resulted in no observable change, establishing the EO was required for the observed activity. The round shape and localization of these beads of polymer indicated that they came from individual active sites, or a localized cluster of neighboring active sites. Thus, the active crystals were not uniformly active or coated uniformly in polymer, but active at specific sites. These bursts, which accounted for all the observable quantity of PEO, were present on less than 10% of particles after 4 h and less than 20% of particles after 14 h. A small number of highly active initial sites occur per sample and per particle (averaging less than 1 site/particle), providing information about the distribution of active sites that would be unobtainable by a bulk-materials measurement. Thus, optical microscopy data is consistent with a heterogeneous polymerization pathway for **1** with ethylene oxide²³ and also identified individual loci of activity.

We next switched to studying catalyst **2**, where the single-crystal morphology and larger crystal size facilitated kinetics measurements. For better observation of crystal surface features, the images were acquired in inverted mode (illumination source reflected off the crystal surface) and with a Raman-equipped microscope to provide spectroscopic characterization. Figure 2 shows one crystal of **2** with two active loci of activity, at the top and bottom of the crystal, observable as darkened regions expanding over the crystal surface with time. Although many (>30) observations of growth on different crystals did not identify obvious crystal face selectivity for the site of initiation, the growth followed pre-existing ridges on the face of the crystal that were observable at 20 \times magnification (example; Figure 2).

Three hypotheses were considered for the composition of the darker regions of growth in Figure 2 (eq 2): (1) chemically or physically wetted surface of crystals of **2** by EO, or solubilized **2** in a microscopic layer of EO, forming potentially reversible polymerization intermediate state **3**, (2) formation of PEO, or (3) a combination of **3** and **4**.



To differentiate between these options, the darkened regions were probed by in situ Raman spectroscopy during their growth phases. Raman spectroscopy with spatial mapping characterized the darkened regions as PEO or EO bound to metal, due to the signature broad C–H band at 2890 cm^{-1} (Figure 3). This

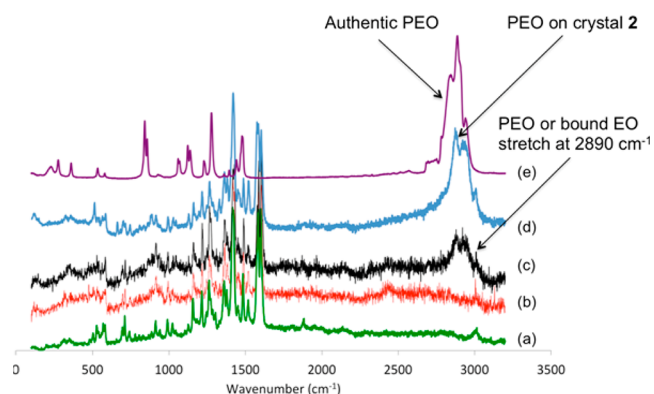


Figure 3. Raman spectra of crystals of **2** under three conditions: (a) in absence of EO, green line; (b) under reaction conditions in presence of EO but nonreacted “white” region of crystal, red line; (c) under reaction conditions, dark region, black line shows characteristic C–H PEO or metal-bound EO stretch; (d) dark region after it grew past the crystal borders; (e) commercially available PEG-OMe.

established change from free EO²⁴ (at 3018 cm^{-1}) is shared by EO bound to silver surfaces²⁵ and is coincident with the shift in solid PEO in the absence of metals.²⁶ EO could be bound to the cobalt center in intermediate stage **3**, producing a similar Raman shift to that reported for EO binding to silver.²² Thus, the darkened regions can be confirmed as containing the C₂H₄O unit, but Raman spectroscopy cannot unambiguously distinguish between **3** and **4**.

At longer reaction times this darkened region grew into PEO beyond the bounds of the original crystal edges, as was observed previously with PEO growth on crystals of **1**. This optically transparent material clearly exhibited the Raman spectroscopy peaks for PEO: the larger amount of material provided higher-signal-to-noise and thus resolution of the multiple signature PEO peaks²³ in the $2600\text{--}2950 \text{ cm}^{-1}$ region than was available at early reaction times.

On about 5 crystals out of >30 monitored with time, the darkened regions both increased and decreased in size over time. This observation is most consistent with assignment of some of the dark regions as reversible intermediate state **3** or as the irreversibly formed polymer **4** changing shape in the unobservable *z*-axis. Thus, assignment of the dark regions as either **3** or **4** or a combination cannot be unambiguously determined at this point; however, its presence on the reaction pathway is confirmed by its requisite appearance prior to the polymer formation that extended beyond the original edges of the crystal and which was characterized unambiguously as PEO by Raman spectroscopy (vide supra).

The kinetics of growth on the crystal surface was estimated by recording the growth of the 2D area with time; thus thickness along the *z*-axis was not included in the estimate

because of the 2D x,y geometry observable through this technique. The graph of the kinetics of expansion at the top active locus in Figure 2 is shown in Figure 4. This rate data

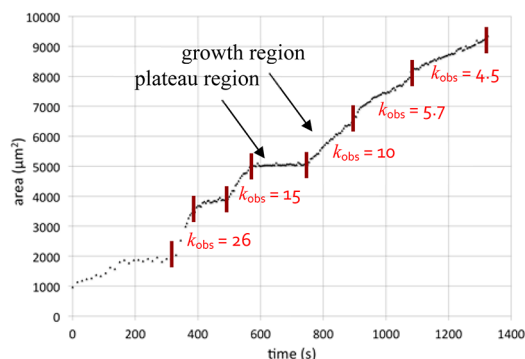


Figure 4. One locus: Graph of growth kinetics estimated in μm^2 for the top active site in Figure 2, showing higher and lower growth rates interspersed by plateaus.

reveals that the locus is *not uniform* in its activity with respect to time but rather cycles through discrete stages of fast expansion and slow expansion. Based on the Raman spectrum shown in Figure 3c this growth is either intermediate state 3 or polymer 4.

The dependence of size on time exhibits several linear growth regions separated by plateaus when no growth occurs. This linear growth is consistent with pseudo-zero order kinetics wherein the effective concentration of EO and catalyst were constant. Six discrete linear growth regions corresponding to six different k_{obs} were detected. After 200 s, the slopes of linear regions decreased with each discrete region. Linear fit of the different growth regions after 200 s provided the pseudo-zero order kinetic constants $k_{obs} = 26, 15, 10, 5.7, \text{ and } 4.5 \mu\text{m}^2/\text{s}$.

The exact mechanism for this change in rate is not yet known; however, it is analogous to single enzyme kinetics wherein the enzyme switches between conformational states with different activities.²⁷ Plausible explanations for the observed change in rate in this case include reversible ligand-binding inhibition,²⁸ or temporary and cyclical blockage of the monomer from diffusing to the active site by the growing polymer. The last hypothesis may explain why k_{obs} decreases with time. It is postulated, for example, that polypropylene does not fully block propylene monomer diffusion into the active site in mesoporous silica with embedded titanocene catalysts in spite of the growing polymer apparently covering the entrance to the mesopores.²⁹ The possibility that the microscope coverslip is contributing to the observed kinetics by physically pressing against the wetting surface or growing polymer (e.g., in a process similar to that which might occur at the walls of reactors) cannot be ruled out at the time. Regardless of the mechanism, the stepwise kinetics provide microscale insight into the polymerization process. To our knowledge, this is the first optical microscopy observation of a stepwise process at individual crystals of an epoxide polymerization catalyst.

In conclusion, the catalysts exhibit single loci of activity, and only a small number of the crystals of **1** (<20%) show high initial activity. Finally, each individual locus in **2**—a single site or collection of neighboring sites—displays stepwise kinetics in the growth of intermediate state 3 or PEO **4**, which is the fingerprint of single-site or small clusters of active sites.^{30,31} If PO reacts similarly to EO, these results suggest that the

reactivity and thus high isotacticity of polymerization of *rac*-PO by **1**¹⁸ could arise from the stereoselectivity of a tiny fraction of the potential sites.

These conclusions arise from the single-crystal resolution of the technique and would not be available through a traditional bulk-materials measurement. While offering less sensitivity than some of the prior spectroscopic and microscopic approaches,^{10–15,32} significant advantages of this approach are the capability to monitor the reaction in situ coupled with the ready availability of inexpensive bright-field optical microscopes, and absence of the requirement for specialized laser instrumentation or training. The challenge in determining reactivity distribution on heterogeneous catalyst surfaces under catalytic conditions with in operando methods is widespread³³ in both industrial^{3,4,34} and academic^{1,18} settings. The reactivity information provided herein suggests that in operando bright-field optical microscopy has been underused compared to its ready availability.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and synthetic procedures and Raman spectroscopy data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-08ER15994), for funding. We thank Prof. Geoffrey W. Coates and Mr. M. Ian Childers for a sample of catalyst **2**.

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