

To Dynamic or To Steady State: When does Non-Steady State Operation lead to Enhancement in the Catalytic Oxidation of Ethane?

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Highlights

- Steady state and dynamic features for ethane oxidation over VO_x and MoO_x catalysts are compared.
- Catalytic functions of chemisorbed (O*) and lattice (O_L) oxygens are elucidated.
- Criteria for dynamic enhancement are evaluated on the basis of O*/O_L ratios.

1. Introduction

Catalytic partial oxidation reactions such as the oxidative dehydrogenation of ethane (ODHE) provide much needed low-temperature pathways for converting light alkanes to value-added chemical products. Forced dynamic operation has been proposed as a means for enhancing olefin or oxygenate selectivity in these oxidation processes that are currently limited by carbon loss through side product formation [1]. Although approaches for mitigating CO_x formation have been presented previously in the literature, the precise mechanistic basis for the observed enhancement in dynamic performance remains unclear. In this study, we provide, for the first time, an explanation of dynamic ODHE enhancement that is grounded in a quantitative analysis of the density and reactivity of chemisorbed (O*) and lattice (O_L) oxygen species on supported VO_x and MoO_x catalysts. The preferential depletion of chemisorbed oxygens is revealed to be a key criterion for dynamic enhancement, with an asymmetry in modeled O*/O_L ratios under dynamic conditions relative to steady state ones providing a lens into the mechanistic basis for dynamic enhancement. Our study establishes a quantitative, molecular-level basis for dynamic enhancement during ODHE, and points to dynamic and steady state O*/O_L ratios as a salient variable that provides unique levers for mitigating side-product formation through forced dynamic operation.

2. Methods

γ -Al₂O₃ supported metal oxide catalysts were synthesized using incipient wetness impregnation. Flow reactor studies were carried out in a 4mm ID quartz tube reactor, with temperature control achieved using a tube furnace and measured with thermocouples at the bed inlet and outlet. Concentration feed forcing was achieved using two 4-way actuator valves from VICI Valco. Catalyst reducibility was assessed using CO temperature programmed reduction (TPR) experiments in which samples were reduced under a 10% CO in N₂ flow while increasing the bed temperature from 25 to 550°C at a ramp rate of 10°C per minute, with the molar flow rate of CO₂ at the bed outlet being quantified using mass spectrometry. Carbon selectivity values as a function of ethane conversion were determined by varying catalyst weight and total flow rate between 0.5 and 10 mg/sccm. A pseudohomogeneous reactor model was used to analyze the step change data, and data fitting was conducted using the Trust Region Reflective algorithm for bounded minimization of the objective function. 95% confidence intervals were determined from an approximation of the covariance matrix and a proper t-statistic parameter, as detailed previously [2].

3. Results and discussion

Dynamic ethylene selectivities for MoO_x/Al₂O₃ catalysts, unlike VO_x/Al₂O₃ catalysts, are greater than the corresponding steady state values any given value of ethane conversion, with the gap between steady state and dynamic selectivities widening with increasing O₂ concentration (Figure 1A). We rationalize these differences in selectivity as arising from the greater oxygen pressure dependencies of unselective deep oxidation reactions compared to the selective ODHE reaction. A detailed kinetic model accounting for partial and deep oxidation reactions over lattice and chemisorbed oxygens, as shown in Figure 1B,

is used to analyze steady state and dynamic kinetic data including the step change data shown in Figure 2. O^* and O_L species on VO_x catalysts exhibit similar reducibilities (as shown using CO TPR) and similar depletion rates (as shown in Figure 2A), unlike those on MoO_x catalysts that exhibit highly dissimilar properties (Figure 2C). Kinetic model parameters derived from steady state and transient data indicate that whereas lattice oxygens on VO_x catalysts effect both of the primary oxidation reactions of ethane i.e. those to ethylene and to CO_x , lattice oxygen species in MoO_x catalysts only contribute to the selective ODHE reaction that produces ethylene. These highly contrasting active site requirements contribute to the distinct O_2 pressure dependencies, and to dynamic enhancement on MoO_x but not VO_x catalysts. Effects of oxide loading, modulation frequency, and O_2 pressure were also evaluated, with $O^*:O_L$ ratios used to identify catalysts and reaction conditions that result in dynamic enhancement.

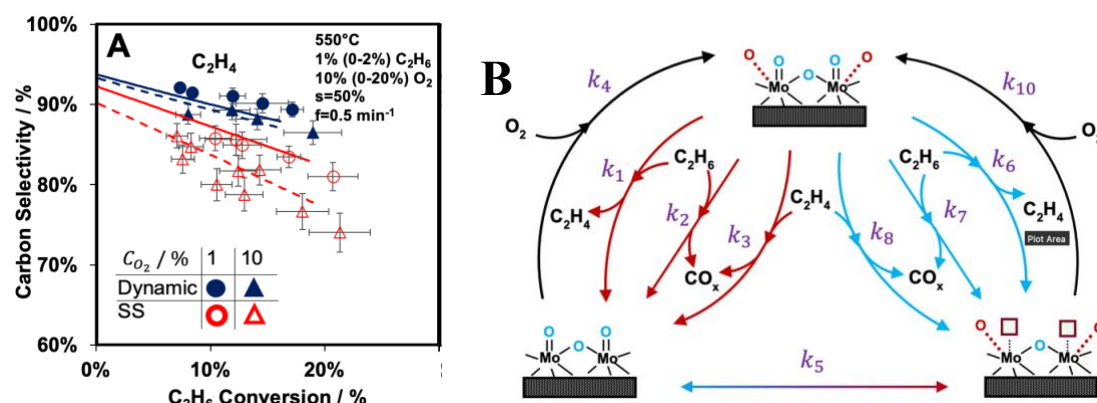


Figure 1. A) Dynamic and steady state C₂H₄ carbon selectivities as a function of C₂H₆ conversion at 550°C and 1 and 10% O₂ for a 0.2 monolayer MoO_x/Al₂O₃ catalyst under 1% C₂H₆; lines through data indicate model predictions. B) Reaction pathways used in the kinetic model with chemisorbed (red) and lattice (blue) oxygens.

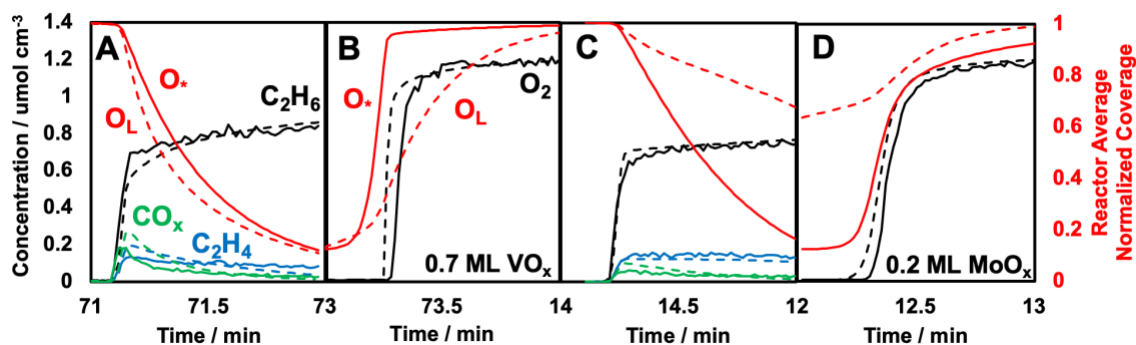


Figure 2. Step change reduction and re-oxidation experiments for 0.7 monolayer VO_x (A-B) and 0.2 monolayer MoO_x/Al₂O₃ at 550°C with cyclic average concentrations of C₂H₆ and O₂ of 1%. For reactant and product concentrations, solid lines represent experimental data and the dashed lines represent model predictions, and for the oxygen coverages, solid and dashed lines denote chemisorbed (O^*) and lattice (O_L) oxygen coverages.

4. Conclusions

In this work, we develop a molecular-level understanding of the criteria for selectivity enhancement during forced dynamic operation of supported VO_x and MoO_x ODHE catalysts. Effects of metal identity, oxide loading, modulation frequency, and O₂ pressure are rationalized on the basis of the ratios of chemisorbed to lattice oxygens, with each of these oxygen species inferred to play contrasting roles on the two classes of catalysts considered. The concepts and criteria used herein to analyze dynamic enhancement can readily be extended to other partial oxidation reactions of industrial importance.

References

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Keywords

Oxidative dehydrogenation; oxide catalysis, forced dynamic operation, chemisorbed and lattice oxygen.