Analysis of Dynamics and Mechanisms of Chemical Reactions (Bridging the Gap: Selective Oxidation of *n*-Butane to Maleic Anhydride at Steady-State and Non-Steady-State Conditions)

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Introduction

The conversion of *n*-butane to maleic anhydride (MA) process over vanadium phosphorous oxide (VPO) catalysts is the only industrially practiced heterogeneous selective oxidation involving an alkane. The selective conversion of alkanes to oxygenates has great practical significance because alkanes are lower-cost feedstocks than their olefin counterparts, and are currently under utilized [1-3]. A fundamental understanding of how VPO catalysts function would provide important insight into the development of new classes of catalytic materials for alkane oxidation.

A key unanswered question in the selective oxidation of *n*-butane to MA over VPO catalysts is the nature of the active-selective phase or phases. Although there is evidence to suggest that $(VO)_2P_2O_7$ is an essential element in active-selective VPO catalysts, it is still unclear how the $(VO)_2P_2O_7$ lattice supplies the 7 oxygen atoms needed to convert *n*-butane to MA [4]. The Temporal Analysis of Products (TAP) reactor system [5,6], can be operated under both steady-state (atmospheric flow experiments) and non-steady-state (vacuum pulse response experiments) conditions to obtain fundamental kinetic information that can be directly related to the catalyst composition under two different pressure regimes. The primary objective of this study is to relate reaction kinetics for molecular level processes to surface processes at more realistic process conditions using the TAP reactor system by operation in different pressure regimes. The data will be used, along with fundamental transport-kinetic models, to quantify the role of oxygen adspecies adsorption on the VPO catalyst, and to explain the mechanism for transport of oxygen atoms from either the bulk or surface sites to the selective oxidation reaction under different reaction conditions.

Materials and Methods

Reactor equilibrated VPO catalysts (~250 micron-sized particles) were packed in a thin zone in the middle of the TAP microreactor surrounded by inert quartz particles of similar size. Atmospheric flow experiments were performed first by introducing a flow mixture of oxygen, argon, and *n*-butane in the ratio 7:1:1 respectively, through a continuous valve into the microreactor. Scan data was taken at a series of reactor temperatures from 385–495 ˚C to observe *n*-butane conversion to products, mostly MA and CO_2. TAP pulse response experiments were then performed by introducing reactant mixtures of *n*-butane/Ar, and reaction intermediates, such as furan/Ar, butadiene/Ar, and 1-butene/Ar, in a reactant to inert ratio of 7:3. Prior to each pulse response experiment, the catalyst was oxidized using a flow of O_2/Ar at 480 ˚C. This was repeated for a series of reactor temperatures from 400 – 480 ˚C. Each pulse of reactant mixture sent into the microreactor represents approximately 10^{14} gas molecules/pulse.

Results and Discussion

In both the steady-state and non-steady-state experiments, it was found that the activity and selectivity of the VPO catalysts improve significantly when the surface of the catalyst is oxidized by an atmospheric flow of oxygen prior to reaction with *n*-butane. This was used to identify optimal conditions for oxygen pretreatment

Results of multi-pulse experiments indicate that there is an optimal oxygen surface concentration needed to yield a maximum in MA production. This occurs when the oxidized VPO surface is reduced by approximately 15 furan pulses (Figure 1). Another feature found from the non-steady-state experiments was that the maximum product yield of MA occurs at the lowest reactor temperature taken, 400 ˚C. Below 400 ˚C, the MA production decreases due to the decrease in the rate of reaction.

These results are explained based on mechanisms with two types of active sites described in previous papers [1-3]. These sites are distinguished by the total numbers and apparent activation energies. Physico-chemically, these sites may differ by the vanadium oxidation degree and/or combination of the different surface structures. Estimation of number of active sites for both types was performed using a theoretical expression $N = N_p [(1-x) x^2] /(C S)$, where N is a number of active sites, N_p is a number of molecules per pulse, x is the conversion, S is the catalyst surface, and C is the slope of the dependence of conversion on number of pulses.
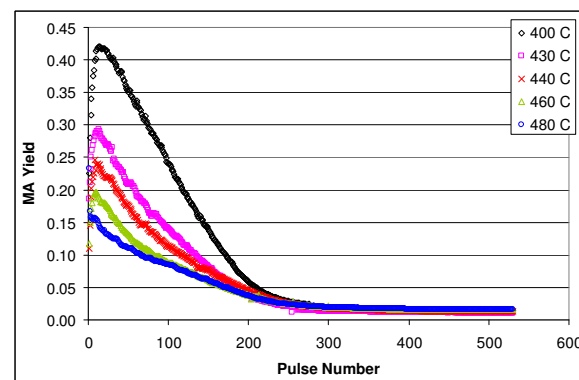

Figure 1. TAP vacuum pulse response data for MA yield as a function of the pulse number for reactor temperatures between 400 – 480 ˚C using furan as the reactant.

Significance

The data and models provides a direct link between kinetic studies for the selective oxidation of n-butane to MA over VPO catalysts at steady-state and non-steady-state conditions, and explain how changes in reaction conditions translate into differences in the observed catalyst performance. This is useful for developing new fundamental reaction mechanisms and for eventually creating new catalysts for commercial applications.

References
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