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Reaction kinetic analysis of the gas-phase epoxidation of propylene over Au/TS-1

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Abstract

The superior activity and stability of Au/TS-1 catalysts has allowed the first comprehensive kinetic analysis of the propylene epoxidation system in the absence of significant deactivation. A unique design of experiments combining the best features of factorial experiments with one-at-a-time experimentation over the nonflammable range was used to collect kinetic information, from which a power rate law was extracted using the statistical software package JMP. Explaining the resultant fractional reactant orders ($O_2 = 0.31 \pm 0.04$, $H_2 = 0.60 \pm 0.03$, and $C_3H_6 = 0.18 \pm 0.04$) requires a sequence of elementary kinetic steps having a minimum of two active sites participating in the rate-determining step. A reaction sequence is proposed that accounts for the experimentally determined reaction orders and is consistent with DFT calculations and other results from the literature. This mechanism suggests that titanium and gold sites must generate and use the epoxidation oxidant simultaneously rather than sequentially, as previously suggested in the literature.

Keywords: Kinetic analysis; Propylene epoxidation; Gold catalysts; Titanium silicalite-1; TS-1; Design of experiments; Propylene oxide

1. Introduction

With the discovery of propylene epoxidation activity in the Au–Ti system by Haruta et al. [1], considerable effort has been made to understand the nanoscale gold particle size effects [1–4] and the elemental synergy between gold and titanium that result in this unique selective oxidation activity [1,5–8]. Although an enhanced understanding of the chemical and physical properties of these materials has recently led to catalysts with industrially interesting propylene epoxidation rates [9,10], mechanistic information derived from kinetic experiments has been limited, due in part to the poor stability and reproducibility of many catalysts in the Au–Ti system. With the introduction of catalysts consisting of highly dispersed titanium centers and low gold loadings, the on-stream stability has improved considerably, culminating in Au/TS-1 catalysts capable of the stable production of propylene oxide (PO) for periods exceeding 45 h [10]. Nevertheless, reproducibility problems in catalyst synthesis prevent direct comparison of activity based on metal loading or gold particle size. In addition, the need for two reductants and an oxidant for the reaction entails safety considerations. Traditional experimental methods involving the manipulation of one reaction variable at a time make it necessary to operate at process conditions remote from a standard feed of 10/10/10/70 vol% $O_2/H_2/C_3H_6$/diluent, to have a sufficiently large range of compositions outside of the explosion limit conducive to estimating reliable reaction orders. The kinetic parameters provided by Haruta et al. [1], for example, were obtained from kinetic information far from the standard evaluation conditions, which raises the question of whether data collected under these conditions necessarily reflect the kinetics of the more widely studied 10/10/10/70 vol% $O_2/H_2/C_3H_6$/diluent reactant mixture.

This work takes advantage of the high activity and stability of catalysts prepared by deposition precipitation of gold onto titanium silicalite-1 to determine reaction orders, rate constants, and apparent activation energies from a large number of variable levels. It has ultimately allowed the proposal of a viable

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epoxidation mechanism over these materials. Utilization of a design of kinetic experiments in which all manipulated variables are changed simultaneously permits the examination of a wide range of nonflammable reaction conditions near the standard evaluation conditions. Another attribute of this design is the ability test for the effects of deactivation and/or catalyst reproducibility. Finally, the experimental design is inherently efficient and permits evaluation of the entire experimental region in a balanced fashion with the ability to check for any synergisms or interactions among the reaction conditions and resultant model parameters.

2. Experimental

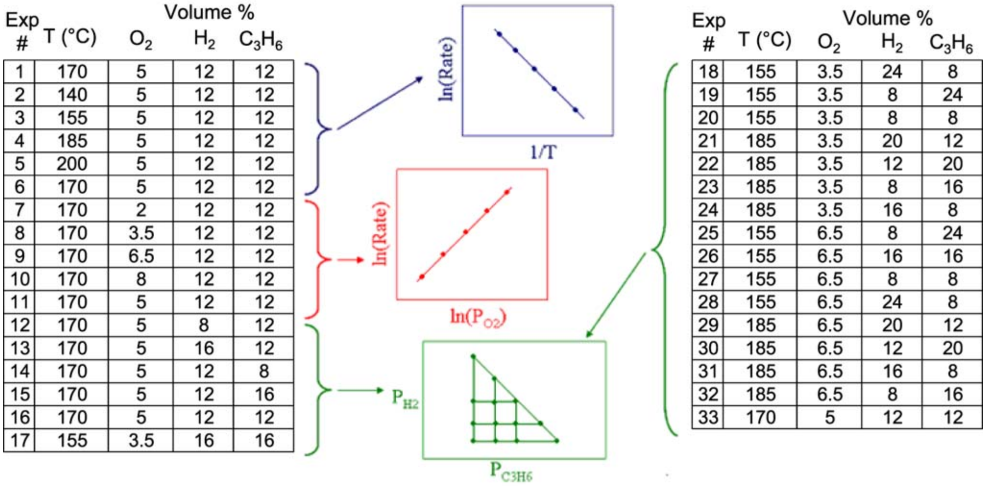
2.1. Hybridized factorial design of experiments

An experimental design was constructed to meet the following requirements: (1) easily attained feed conditions, (2) measurable changes in expected product rates, and (3) operations maintained outside the flammability region. Based on exploratory experimental observations, the oxygen concentration ranged from 2 to 8 mol%, whereas the hydrogen and propylene concentrations ranged from 8 to 24 mol%. In addition, Au/TS-1 catalysts temperatures ranged from 140 to 200 °C. Higher temperatures were not examined because of irreversible deactivation of the catalyst. Lower temperatures were neglected to avoid confounding the kinetics with the accumulation of PO on the surface. Based on exploratory experiments, the choice was made to use 15 °C increments over this 60 °C temperature range.

The design itself consists of a hybridization of a factorial design and the traditional one-at-a-time approach familiar to catalyst experimenters. As shown schematically in Fig. 1, the first portion of the design consists of incremental changes in temperature under constant reactant compositions, which can be used to give estimates of the activation energy and pre-exponential factor using a logarithmic transformation. The second portion of the design consists of step changes in oxygen compositions, resulting in the ability to extract an effective oxygen order independent of other factors. The final portion of the experimental design consists of a symmetrical partial factorial design for hydrogen and propylene that has been linked to the first two portions through the use of intermediate temperatures and concentrations. The design consisted of 29 distinct reaction conditions, plus 4 replicates to assess experimental error and check for catalyst deactivation. The reaction conditions (5/12/12/71 vol% $O_2/H_2/C_3H_6$/diluent, 170 °C) were chosen as the replicate conditions because they consist of roughly midpoint values of the four process variables. It was felt that repeating this middle point would serve as a good measure of variability over the entire operating region.

2.2. Catalyst preparation and characterization

Two titanium silicalite-1 samples were synthesized in micellar media [11] and named according to the silicon-to-titanium molar ratio such that Si/Ti = 36 is denoted by TS-1(36) and Si/Ti = 143 is denoted by TS-1(143). The specifics of the preparation, as well as the characterization of these support materials, have been presented previously [10]. A typical synthesis gel began with the addition of 3.5 g of polyoxyethylene 20-sorbitan monolaurate (Tween® 20, Fischer Scientific, Enzyme Grade) to 56 mL of deionized water under vigorous stirring. This was followed by dropwise addition of 26 mL of tetrapropylammonium hydroxide (TPAOH, Aldrich, 40 wt%), followed by dropwise addition 66.5 mL of tetraethylorthosilicate (TEOS, Aldrich, >98%). The solution was then stirred for 1 h. A solution consisting of up to 3 mL of titanium (IV) butoxide (TBOT, Aldrich, >98%) in 20 mL of isopropyl alcohol (IPA, Mallinckrodt, ChromAR) was then added dropwise under stirring. The final solution was stirred for a minimum of 1 h before being placed in a Teflon autoclave at 140 °C for 18 h. The resulting solid was separated from the growth liquid via centrifugation, washed thoroughly with approximately 100 mL of room temperature deionized water, and dried overnight at room temperature in a vacuum oven. Once dry, the resulting white



Exp #	T (°C)	Volume % O$_2$	H$_2$	C$_3$H$_6$
1	170	5	12	12
2	140	5	12	12
3	155	5	12	12
4	185	5	12	12
5	200	5	12	12
6	170	5	12	12
7	170	2	12	12
8	170	3.5	12	12
9	170	6.5	12	12
10	170	8	12	12
11	170	5	12	12
12	170	5	8	12
13	170	5	16	12
14	170	5	12	8
15	170	5	12	16
16	170	5	12	12
17	155	3.5	16	16

Exp #	T (°C)	Volume % O$_2$	H$_2$	C$_3$H$_6$
18	155	3.5	24	8
19	155	3.5	8	24
20	155	3.5	8	8
21	185	3.5	20	12
22	185	3.5	12	20
23	185	3.5	8	16
24	185	3.5	16	8
25	155	6.5	8	24
26	155	6.5	16	16
27	155	6.5	8	8
28	155	6.5	24	8
29	185	6.5	20	12
30	185	6.5	12	20
31	185	6.5	16	8
32	185	6.5	8	16
33	170	5	12	12

Fig. 1. A schematic showing a breakdown of the hybridized factorial design of kinetic experiments. The first two portions of the design are similar to traditional kinetic analysis in which only one variable is changed at a time, while the final portion is a true factorial design.