Mechanisms for C—C bond cleavage and formation during acrolein production on a mixed metal oxide catalyst

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ABSTRACT

We report a reaction network detailing the mechanistic origins of 20 C_2–C_6 byproducts observed during the oxidation of propylene to acrolein at 623 K on a molybdenum-based catalyst promoted with cobalt and nickel used in the industrial production of acrolein. The carbon backbone of propylene is preserved in the sequential oxidation of propylene to allyl alcohol, acrolein, and acrylic acid, as well as propylene oxidation to acetone and propanal via water-mediated pathways. Transient kinetic measurements in conjunction with co-feed experiments of C_2 and C_3 aldehydes and carboxylic acids show that decarbonylation and decarboxylation reactions, reactions of organic compounds with surface-adsorbed oxygen species, and total combustion reactions are the three mechanisms for C—C bond cleavage. C—C bond formation reactions that result in C_4–C_6 byproducts occur via: (i) the addition reaction of a propylene-derived surface allyl species with formaldehyde to form C_4 products and with propylene and allyl alcohol to form C_6 products, or (ii) the addition reaction of an acrolein (acrylic acid)-derived surface ethenyl intermediate with propylene to form pentadiene and with acrolein to form C_5 cyclic oxygenates.

1. Introduction

The partial oxidation of propylene to acrolein on multi-component metal oxide catalysts constitutes the first step in upgrading propylene to high valued acrylate-based polymers and chemicals [1]. The oxidation of propylene on Bi-Mo-based formulations generates C_1–C_3 aldehydic and acidic compounds as major side products including but not limited to CO, CO_2, formaldehyde, acetaldehyde, acetic acid, allyl alcohol, and acrylic acid [2,3]. The minor byproducts of this process consist of C_4 and higher oxygenates and hydrocarbons [4]. These compounds, even at ppm level concentrations, adversely affect the production of acrolein and acrylic acid by inducing the formation of high-boiling point tarry compounds, causing fouling in the reactor, plugging transfer lines, and deteriorating desired product quality [4].

The catalytic cycle for acrolein synthesis, as proposed by Grasselli et al. [5] and later by Zhai et al. [6], follows a Mars-van Krevelen-type mechanism and comprises the following sequence of steps: (i) activation of the allylic C—H bond in propylene to form a surface allyl intermediate, (ii) incorporation of a lattice oxygen to the propylene-derived allyl species, (iii) cleavage of a C—H bond of the allyloxide species followed by acrolein desorption to generate a lattice vacancy site, and (iv) surface reoxidation with gas-phase oxygen. Results from steady-state kinetic measurements of propylene oxidation [6–8], oxidation

reactions of allyl alcohol, allyl azide, and allyl iodide as probe molecules [9,10], isotopic tracer experiments with deuterated propylene and allyl alcohol and, separately, oxygen-[18]O [10–13], and DFT calculations [14–16] all support this mechanism. Based on mechanistic proposals for gas-phase reactions analogous to the ones involved in acrolein synthesis, Wong et al. [17] postulated an elementary-step kinetic model describing the formation and consumption of acrolein on a metal oxide catalyst with two acrolein-derived surface species [$CH_2 = O$] and [$CH_2 = CHO$] as the major precursors for the formation of side products including acrylic acid, acetone, acetaldehyde, acetic acid, formaldehyde, formic acid, CO, and CO_2. In a recent report [3], we developed a detailed reaction network and kinetic model that rigorously captures the formation and consumption of all C_3 and smaller products during propylene oxidation on $Bi_2Mo_3O_{12}$ at 623 K and proposed decarbonylation of aldehydic compounds, decarboxylation of carboxylic acids, and reactions of organic compounds with surface-adsorbed oxygen species as the three primary mechanisms for the formation of C_1 and C_2 products. In the same report, we proposed the existence of four different types of active sites on the surface of $Bi_2Mo_3O_{12}$ during propylene oxidation to acrolein: (i) nucleophilic lattice oxygen, (ii) electrophilic adsorbed oxygen, (iii) surface hydroxyl groups, and (iv) active sites for decarboxylation of carboxylic acids. The precursors and mechanisms for the formation of C_4 and higher byproducts on industrially

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relevant catalysts, however, remain elusive.

In this work, we report the evolution of product selectivity as a function of propylene conversion and initial synthesis rates of 20 C_2–C_6 products observed at carbon selectivities > 0.0001% during propylene oxidation at 623 K in the presence of different co-fed probe molecules on a molybdenum-based catalyst promoted with cobalt and nickel. The reaction rates were assessed under conditions that permit strict kinetic control at high propylene chemical conversions (0–70%) in a gradient-less recirculating batch reactor. We elucidate the reaction mechanisms, identify the existence and involvement of relevant surface intermediates, and develop an extensive reaction network describing the formation of all C_2–C_6 products and illustrating the underlying mechanisms for C—C bond cleavage and formation reactions. C—C bond cleavage reactions that lead to the formation of C_2 and C_1 products are shown to occur via three mechanisms: (i) the decarbonylation of aldehydes and decarboxylation of carboxylic acids, (ii) total oxidation reactions, and (iii) reactions of organic compounds with surface-adsorbed oxygen species. The formation of C_4 products (butadiene, crotonaldehyde, methyl vinyl ketone) is shown to occur via addition reactions between a propylene-derived surface allyl (C_3H_5) intermediate and formaldehyde. Similarly, C_6 byproducts (hexadiene, benzene) are formed via addition reactions of the same allyl (C_3H_5) species with propylene and allyl alcohol. C_5 products (methylfuran, furfural, pentadiene), on the other hand, are synthesized via an acrolein-derived surface ethenyl (C_2H_3) species in its reactions with acrolein and propylene. These mechanistic insights can guide process conditions and catalyst development to minimize the formation of undesired products.

2. Materials and methods

Catalytic reactions were performed in a recirculating batch reactor on a packed catalyst bed in a quartz tube (0.4 cm inner diameter, 0.32 cm^3 catalyst bed volume) equipped with a K-type thermocouple penetrating the axial and radial centers of the catalyst bed. Isothermal reaction conditions were maintained using two cartridge heaters (Omega Engineering Inc., CIR-2100, 600 W) inserted inside two split-tube aluminum sleeves regulated by a Watlow temperature controller (96 Series). Intra-particle and inter-phase mass and energy transport limitations, as well as transport limitations within the catalyst bed, were negligible as assessed by criteria originally proposed by Mears [18], Anderson [19], and Weisz-Prater [20] (Section S.1 of Supporting Information). The total volume of the reactor was 535 cm^3. A syringe pump (KDS Scientific, KDS-100) was employed to introduce the liquid to the feed. The inlet of the liquid port was maintained at 383 K, while all transfer lines was maintained at 433 K, which is above the boiling temperature of all co-feed molecules, to prevent condensation of the reactants and products. Our carbon balance closed within 98% for all experiments, indicating that condensation of reactants or products was absent.

Catalyst particles with sizes between 180 and 425 μm (80 − 40 mesh) were obtained by pressing and sieving the catalyst powder. The catalyst bed was heated to 623 K from ambient conditions with a rate of 0.083 $K\,s^{-1}$ in dry air (0.83 $cm^3\,s^{-1}$ at NTP conditions) prior to kinetic measurements. The catalytic oxidation of propylene was performed at 623 K with 13.0 mg catalyst diluted in 300 mg quartz sand (180 and 425 μm) with an initial feed composition of 7.5 kPa propylene (99.99%, Matheson TriGas), 57 kPa air (21% oxygen and 79% nitrogen, Ultra Zero Certified grade, Matheson TriGas), 9 kPa water (de-ionized), and 89 kPa helium (grade 4.7, Minneapolis Oxygen Company). For co-feed experiments, 0.1–1.0 M solutions of the following compounds were prepared in de-ionized water: formaldehyde (methanol-free, 16 wt/v% in water, Thermo-Scientific), acetaldehyde (99.5%, Sigma-Aldrich), propanal (99.5%, Sigma-Aldrich), acetone (99.7%, Sigma-Aldrich), acetic acid (99.5%, Sigma-Aldrich), acrylic acid (99.7%, Sigma-Aldrich), propionic acid (99%, Sigma-Aldrich), allyl alcohol (99%, Sigma-Aldrich), 1,5-hexadiene (99%, Sigma-

Aldrich). The initial molar ratio of the co-feed and water in the reacting mixture as assessed by gas chromatography always matched that of the stock solution. Acrolein was fed as a gas mixture of 2% acrolein and 16% nitrogen in helium (Matheson Trigas). For isotopic tracer experiments, propylene-$^{13}C_3$ (99 atom% ^{13}C, Sigma-Aldrich) was used.

The initial reactant mixture with and without co-feeds was recirculated at 7 $cm^3\,s^{-1}$ in the reactor for ∼30 min using a micro-recirculating pump (Metal Bellows, MB-21) before being diverted to the catalyst bed. The contents of the reacting gas mixture were sampled at three-minute intervals using a multi-position valve (Vici-Valco, EMT6ST16MWE) until 45 min and at 35-min intervals afterwards and were separated using an Agilent 6890 gas chromatograph (GC) equipped with an HP-Plot/Q column (30.0 m x 320 μm x 0.20 μm) for all organic products in series with a MolSieve-5A column (30.0 m x 320 μm x 0.20 μm) for nitrogen, oxygen, and CO. The separated compounds were quantified using a flame ionization detector (FID) for all C_3 and smaller organic compounds, a thermal conductivity detector (TCD) for water, nitrogen, oxygen, CO, and CO_2, and mass spectrometry for all C_4–C_7 products.

The net synthesis rate of a species was estimated by fitting a sextic polynomial to the molar quantity of that species as a function of reaction time and calculating the first order derivative. The net synthesis rate and selectivity of a species were extrapolated to zero propylene conversion to calculate the initial synthesis rate and initial selectivity of that product. The isotopologue distribution of selected organic species was determined from mass fragmentation patterns using the method described by Price and Iglesia [21]. The mass fragmentation patterns were corrected for the natural abundance of ^{13}C atoms following the method described by Moseley [22].

3. Results and discussion

3.1. Product rank and stability analysis

Propylene oxidation over the catalyst used in this study (623 K, initial 7.5 kPa propylene, 12.0 kPa oxygen, 9.3 kPa water) results in the formation of 27 products (at ∼70% propylene conversion) as listed in Table 1. The desired product, acrolein, is formed at ∼88% selectivity. The major side products with selectivity exceeding 0.1% include formaldehyde, CO, CO_2 (C_1 products), acetaldehyde, acetic acid, ethylene (C_2 products), acrylic acid, allyl alcohol, propanal, and acetone (C_3 products). The minor products with selectivity exceeding 0.0001% include butadiene, crotonaldehyde, methyl vinyl ketone (C_4 products), linear isomers of pentadiene, 2- and 3-methylfuran, 2- and 3-furfural (C_5 products), linear isomers of hexadiene, benzene (C_6 products), toluene, benzaldehyde (C_7 products), allyl acrylate, allyl acetate, methyl acrylate, and trace amounts of methanol and acetylene.

The rank of each product in the reaction network and its stability is identified by the trend of its selectivity as a function of propylene conversion. The products are divided into five categories (Table 1 and Fig. 1): (i) primary unstable products with continuously decreasing selectivities from initial non-zero values (e.g. allyl alcohol), (ii) primary and secondary unstable products with selectivities that attain a maximum from initial non-zero values (e.g. acrolein), (iii) primary and secondary stable products with continuously increasing selectivities from initial non-zero values (e.g. acetaldehyde), (iv) secondary unstable products with selectivities that attain a maximum from initial zero (e.g. benzene), and (v) secondary stable products with continuously increasing selectivities from initial zero values (e.g. acrylic acid). Allyl alcohol, propanal, acetone, and hexadiene are identified as primary unstable products, indicating that they are formed directly from propylene and react to generate other products as the reaction progresses.[28] All C_1 products (formaldehyde, CO, and CO_2) are identified as primary and secondary stable products, suggesting that they are formed from the fragmentation and combustion of both propylene and other organic compounds in the system. Acrylic acid and acetic acid appear as