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KINETICS, CATALYSIS, AND REACTION ENGINEERING

Staged O_2 Introduction and Selective H_2 Combustion during Catalytic Reactions of Alkanes on Cation-Exchanged H-ZSM5

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Stoichiometric reactions can be used to remove H_2 and the associated kinetic and thermodynamic barriers that lead to low dehydrocyclodimerization selectivity during alkane reactions on cation-modified H-ZSM5. O_2 co-reactants can form H_2O in exothermic reactions that balance the enthalpy of endothermic dehydrogenation steps. O_2 reacts preferentially with H_2 via homogeneous and heterogeneous pathways, but also with hydrocarbons as H_2 is depleted; thus, it must be gradually introduced as H_2 forms in dehydrogenation reactions. Staged O_2 protocols significantly increased aromatics yields during C_3H_8 reactions on unexchanged and on Ga- and Zn-exchanged H-ZSM5. On Ga/H-ZSM5, the maximum aromatic yields increased from 54% to 68% and aromatization/cracking selectivity ratios increased from 2.1 to 3.9 when O_2 was introduced gradually into a gradientless batch reactor as H_2 formed. O_2 introduced was converted to H_2O with >95% selectivity; an equivalent amount of O_2 initially added with C_3H_8 led to low H_2O selectivities (<60%). Similar effects of O_2 addition and of staging protocols were observed for alkane reactions on H-ZSM5 and Zn/H-ZSM5. Staging strategies led to selective use of O_2 to remove thermodynamic and kinetic bottlenecks and to unprecedented aromatics yields during alkane reactions on cation-exchanged H-ZSM5.

Introduction

The selective conversion of light alkanes to alkenes and aromatics provides an attractive route to useful chemicals and fuels. The presence of exchanged cations, such as Ga,[1−10] Zn,[11−20] and Pt,[21,22] within shape-selective channels in H-ZSM5 increases the rate and selectivity of alkane dehydrocyclodimerization reactions that form C_6−C_9 aromatics, while decreasing the selectivity to hydrogen-rich unreactive products, such as CH_4 and C_2H_6, which form via cracking reactions. Ga/H-ZSM5 catalysts provide the basis for the CYCLAR process.[23]

Mole et al. first proposed that Zn cations act as hydrogen recombination sites in dehydrogenation steps required to form aromatics.[13] Kinetic and isotopic tracer studies later confirmed this proposal.[7−12] The required bifunctional pathways involve alkane and alkene reactions on zeolitic acid sites and dehydrogenation steps aided by recombinative desorption steps on exchanged Zn, Ga, Co, and other cations. The rate-limiting nature of hydrogen removal steps leads to high hydrogen virtual pressures at catalyst surfaces, which have been measured from the deuterium content in products formed from C_3H_8/D_2 reactants.[18] Exchanged cations increase the rate of communication between surface and gas-phase hydrogen pools by acting as recombinative desorption sites. In this manner, cations favor the formation of hydrogen-deficient adsorbed intermediates, which in turn favor the formation and desorption of dehydrogenation and aromatization products and also of unreactive unsaturated residues that lead to site deactivation.

The hydrogen removal bottlenecks prevalent during alkane reactions on these catalysts limit alkane conversion rates, predominately by reversing the required C−H bond activation steps and by imposing an unfavorable overall equilibrium for the formation of alkene intermediates on surfaces and of aromatic products. As a result, molecules that react with adsorbed hydrogen, with hydrogen-rich intermediates, or with their gas-phase precursors (e.g., H_2) can increase aromatics synthesis rate and selectivity. Fujimoto et al. reported that alkane/O_2 reactant mixtures led to higher aromatic selectivities than pure alkane reactants on H-ZSM5 and Ga/H-ZSM5.[5] Iglesia and Baumgartner showed that O_2, CO, and CO_2 increased the selectivity of propane conversion to aromatics on H-ZSM5[8] by acting as stoichiometric hydrogen acceptors for surface and gas-phase hydrogen species. In all of these studies, O_2 reactions with H_2 lead to higher aromatics selectivity, but a large fraction of the O_2 co-reactants was consumed via unselective hydrocarbon combustion reactions to form CO and CO_2.

Ga/H-ZSM5 and Zn/H-ZSM5 are the most active and selective catalysts for alkane dehydrocyclodimerization. Aromatics yields as high as 53% have been reported on Ga/H-ZSM5[3] using propane reactants and relatively high temperatures (823 K, 1 bar C_3H_8). Zn/H-ZSM5 gives lower reaction rates and aromatics selectivities; the highest reported aromatics yields are below 50%,[19]

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but high aromatics selectivities (>90%) have been reported at very low but unspecified propane conversion levels.[20] These limiting yields as conversion increases reflect the selective kinetic and thermodynamic inhibition of the dehydrogenation pathways required to form aromatics and the concomitant increase in cracking selectivity as H_2 pressures increase with increasing alkane conversion.

Here, we exploit the ability of semibatch reactors with continuous O_2 introduction to conveniently and accurately simulate the behavior of plug-flow tubular reactors with staged O_2 feeds in an effort to determine the kinetic and thermodynamic consequences of concurrent hydrogen combustion during propane reactions on H-ZSM5, Zn/H-ZSM5, and Ga/H-ZSM5. Controlled O_2 introduction strategies led to selective hydrogen combustion and to the removal of the kinetic and thermodynamic bottlenecks that limit aromatics yields. The availability of O_2 only as H_2 is formed is critical in our selective H_2 combustion strategies. We report oxygen staging protocols that increase aromatization to cracking selectivity ratios by a factor of 2 and lead to very selective use of O_2 co-reactants in hydrogen removal and to unprecedented aromatics yields (~70%), even at relatively low temperatures (773 K).

Experimental Methods

Catalyst Synthesis and Characterization. Na-ZSM5 (Zeochem, Si/Al = 14.5) was exchanged three times with a solution of ammonium nitrate (Fisher, Certified ACS, >98.0%) at 353 K for 16 h, then filtered, and washed with deionized water to form NH_4-ZSM5. These NH_4-ZSM5 samples were treated in ambient air at 398 K overnight and then in flowing dry air (Airgas, zero grade) at 773 K for 20 h to form H-ZSM5. Ga cations were introduced onto H-ZSM5 by incipient wetness impregnation using a 0.065 M $Ga(NO_3)_3$ solution (Aldrich, >99.9%). The samples were then dried and treated in flowing dry air at 773 K for 20 h. Previous studies have shown that this procedure leads to Ga exchange as Ga^+ during subsequent reduction in H_2 at 773 K for 1−2 h.[9] Zn/H-ZSM5 samples were prepared by ion exchange of H-ZSM5 with a 0.0065 M solution of $Zn(NO_3)_2$ (Aldrich, >98.0%) at 343 K. The exchanged samples were filtered, washed with deionized water, dried in flowing dry air at 383 K for 20 h, and then treated in flowing dry air at 773 K for 20 h.[12]

Si, Al, Na, and Ga or Zn contents were measured by atomic emission spectroscopy (Galbraith Laboratories, Inc.). H-ZSM5 samples contained traces of residual Na (0.14 wt %; Na/Al = 0.064). Ga/H-ZSM5 contained 1.8 wt % Ga, corresponding to a Ga to framework Al atomic ratio of 0.25. Zn/H-ZSM5 contained 1.0 wt % Zn and a Zn/Al_F atomic ratio of 0.14. The number of residual OH groups, measured by isotopic exchange with D_2, were similar in Zn and Ga samples because of the respective exchange stoichiometries of isolated Ga^+ and Zn^{2+} cations.

Catalytic Reaction Rates and Selectivities. All reaction rate and selectivity measurements were carried out using a gradientless recirculating batch reactor.[7] The reactor contents (520 cm^3) were circulated at >2 $cm^3\ s^{-1}$ to ensure differential reaction conditions (<1% reactant conversion per pass). Catalyst samples (0.05−0.20 g) were treated at 773 K in flowing dry air (Airgas, zero grade) for 1 h before catalytic experiments. Ga/H-ZSM5 samples were also treated in flowing H_2 at 773 K for 2 h; this treatment led to the reduction of unexchanged Ga_2O_3 to form volatile Ga_2O species, which migrate into ZSM5 channels and replace some of the acidic H^+ species in H-ZSM5.[6,10]

Propane reaction rates and selectivities were measured at 773 K using propane (20.0 kPa, Praxair, 99.999%) and three reactant introduction protocols: (i) C_3H_8 reactants (20.0 kPa). (ii) C_3H_8 (20.0 kPa) and O_2 (13.4 kPa) (Scott Specialty Gases, Inc., 99.999%) concurrently introduced at the start of the experiment (*co-feed mode*). (iii) C_3H_8 (20.0 kPa) introduced at the start and O_2 added gradually at a constant rate (0.75−6.6 mmol/g-atom of Al s) (*staged feed mode*). Oxygen staging intensity is defined as the ratio of the total amount of introduced O_2 to that required to consume all of the H_2 formed during alkane reactions. A staging intensity of 1.0 is defined as the *stoichiometric case*.

Ar (1 kPa; research grade >99.9999%) was used as an internal standard and the reactor was initially kept at ambient pressure using He (balance; Airgas, research grade >99.9999%) as an inert diluent. O_2 was introduced via a quartz capillary column (60-m length, 250-μm diameter) at a rate controlled by the pressure imposed by an upstream regulator.

Reactant and product concentrations were measured using on-line gas chromatography (Hewlett-Packard, Model 5890). Samples were collected using a ten-port valve with two sample loops residing within the recirculation path. The samples were injected into capillary (HP-1 methyl-silicone column, 50 m, 320 μm) and packed (Supelco, 1000 Carboxen) columns. Flame ionization was used to detect hydrocarbons eluting from the capillary column. The packed column effluent was analyzed by thermal conductivity to measure Ar, N_2, O_2, CO, and CO_2.

Batch reactor data are shown as product site yields (mol/g-atom of Al). Reaction rates were calculated from the slopes of these data and reported as molar propane conversion rates (total or leading to a given product per g-atom of Al). Rates are calculated from the slopes of the line connecting each point to the origin; these rates correspond to those measured in a mathematically equivalent plug-flow reactor after that residence time. The mathematical analogy between temporal staging of O_2 in a batch reactor and spatial O_2 staging in a plug-flow reactor is described in detail elsewhere.[24]

Hydrocarbon selectivities are reported on a carbon basis as the percentage of the converted propane appearing as a given reaction product. Hydrogen selectivities are reported as the percentage of the hydrogen in the converted propane appearing within each product. Selectivities are also given on an oxygen basis for O_2 introduction experiments; they are defined as the fraction of the O_2 introduced that appears as H_2O or CO_x (CO and CO_2). These oxygen-based selectivities represent a measure of the relative effectiveness with which O_2 is used to combust hydrogen and hydrocarbons.

The approach to equilibrium (η) for each product formation reaction was determined from the thermodynamics of the corresponding stoichiometric reaction, as illustrated below for benzene:

$$C_3H_8 \rightarrow {}^{1}/_{2}C_6H_6 + {}^{5}/_{2}H_2$$

$$\eta = \frac{[P_{C_6H_6}]^{1/2}[P_{H_2}]^{5/2}}{[P_{C_3H_8}]} \times \frac{1}{K_{EQ}}$$

Table 1. Effects of Oxygen Staging on Propane Dehydrocyclodimerization Turnover Rates and Product Distribution in Gradientless Batch Reactors [773 K, 20 kPa Propane, Balance He]

	1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25)				1.0 wt % Zn/H-ZSM5 (Zn/Al = 0.14)				H-ZSM5 (Si/Al = 14.5)			
oxygen introduction rate (mmol of O_2/g-atom of Al s)	0.0		3.3		0.0		1.7		0.0		0.75	
oxygen staging intensity	0.0		1.0		0.0		1.3		0.0		1.6	
propane conversion (%)	31.8	59.5	40.4	61.6	31.3	59.0	32.8	56.3	30.2	58.4	36.5	60.9
propane to hydrocarbons turnover rate (per Al, 10^{-3} s^{-1})	8.1	5.7	8.2	6.0	4.0	3.0	4.0	2.8	3.5	2.4	3.5	2.5
propane to aromatics turnover rate (per Al, 10^{-3} s^{-1})	4.8	3.8	5.6	4.4	2.0	1.8	2.3	1.8	0.57	0.76	0.88	0.92
propane to carbon oxides turnover rate (per Al, 10^{-3} s^{-1})			0.12	0.089			0.12	0.10			0.11	0.11
carbon selectivity (%)												
methane	11.6	12.9	11.8	12.1	19.1	19.2	18.5	19.0	26.4	29.0	25.6	28.7
ethene	6.5	3.3	4.3	2.6	10.2	5.0	10.6	5.2	18.3	9.4	15.2	8.5
ethane	11.0	11.8	10.2	8.4	10.0	11.6	5.9	6.3	13.6	17.1	13.3	15.9
propene	8.5	3.5	4.2	2.9	6.8	2.9	5.6	2.5	14.4	7.2	11.8	6.1
C_4-C_5	3.3	1.4	1.3	0.8	2.7	1.2	2.0	0.8	10.9	5.6	9.1	4.2
C_{6+} aromatics	59.1	67.2	68.2	73.3	51.2	60.0	57.4	65.6	16.4	31.7	25.0	36.7
benzene	25.9	28.7	30.8	34.0	20.3	22.6	23.3	26.3	3.8	8.2	5.8	9.7
toluene	23.4	23.4	22.7	22.2	20.3	21.0	21.0	19.6	6.6	11.6	9.2	12.6
C_8 aromatics	6.7	6.0	4.6	4.7	6.8	6.3	5.9	4.8	3.4	5.2	4.1	5.2
C_{9+} aromatics	3.2	9.1	10.1	12.3	3.7	10.1	7.1	14.9	2.6	6.8	5.9	9.2
hydrogen selectivity (%)												
H_2	30.3	31.7	34.1	36.3	22.6	24.8	29.1	31.3	3.8	6.1	10.1	11.9
oxygen selectivity (%)												
H_2O			96.9	96.7			88.6	87.5			79.4	77.9
CO			1.2	1.3			4.1	4.4			7.2	7.1
CO_2			1.9	2.0			7.3	8.1			13.4	15.0

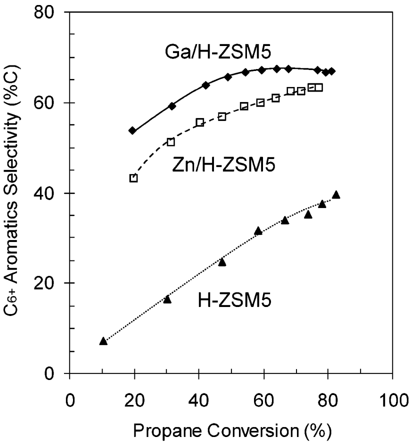


Figure 1. Effects of cations on C_{6+} aromatics selectivity during propane dehydrocyclodimerization in gradientless batch reactors [773 K, 20 kPa propane, balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25); 1.0 wt % Zn/H-ZSM5 (Zn/Al = 0.14); H-ZSM5 (Si/Al = 14.5)].

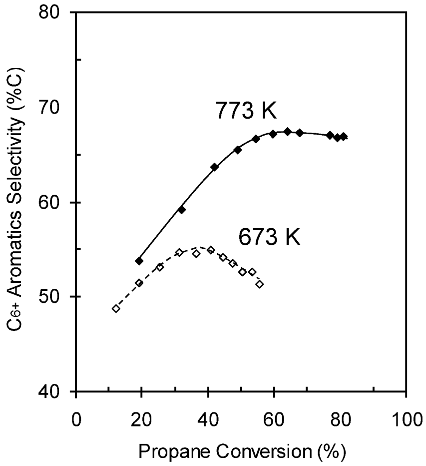


Figure 2. Effects of temperature on C_{6+} aromatics selectivity during propane dehydrocyclodimerization in gradientless batch reactors [20 kPa propane, balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25)].

K_{EQ} are equilibrium constants obtained from literature thermodynamic data.[25] The value of η is zero far away from equilibrium and approaches unity as equilibrium is reached; thus, $(1 - \eta)$ represents the fractional distance from equilibrium for a given reaction, which increases with increasing reaction time.

Results and Discussion

Propane Dehydrocyclodimerization on H-ZSM5, Zn/H-ZSM5, and Ga/H-ZSM5. Ga and Zn cations increased propane turnover rates and the rate and selectivity for aromatics formation (Table 1). These effects are illustrated at two propane conversion levels in Table 1; they reflect the contribution of exchanged cations to hydrogen removal as H_2.[8-12,17,18] The fraction of the hydrogen in the converted propane that appears as H_2 increased significantly as some of the protons in H-ZSM5 were replaced by Ga or Zn cations (Table 1). Reaction selectivities on different catalysts must be compared at similar propane conversions because the sequential nature of dehydrocyclodimerization pathways, the intermediate role of propene, and the approach to equilibrium for some reactions as H_2 forms combine to lead to marked changes in selectivity as conversion increases (Figure 1, Table 1). At all conversion levels, Ga/H-ZSM5 shows the highest C_{6+} aromatics selectivity; these selectivities, however, reach a maximum value of ~67% and then decrease as propane conversions increase above ~60% (Figure 2). These maximum attainable selectivities reflect the stronger kinetic and thermodynamic effects of H_2 concentrations on propane to aromatics reaction rates compared with their effects on the rates of parallel cracking steps. Similar trends were observed at lower temperatures

Table 2. Approaches to Equilibrium during Propane Dehydrocyclodimerization Reactions in Gradientless Batch Reactors [773 K, 20 kPa Propane, Balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25); 1.0 wt % Zn/H-ZSM5 (Zn/Al = 0.14); H-ZSM5 (Si/Al = 14.5)]

	Ga/H-ZSM5		Zn/H-ZSM5		H-ZSM5	
propane conversion (%)	31.8	80.8	31.3	79.5	30.2	82.3
η ($C_3H_8 \rightarrow {}^1/_2C_6H_6 + {}^5/_2H_2$)	2.4×10^{-4}	0.014	8.8×10^{-5}	7.2×10^{-3}	4.0×10^{-7}	1.9×10^{-4}
η ($C_3H_8 \rightarrow C_3H_6 + H_2$)	0.10	0.39	0.056	0.27	0.019	0.18
η ($C_3H_6 \rightarrow {}^1/_2C_6H_6 + {}^3/_2H_2$)	2.4×10^{-3}	0.035	1.6×10^{-3}	0.027	2.2×10^{-5}	1.0×10^{-3}
η ($C_3H_6 \rightarrow {}^3/_7C_7H_8 + {}^9/_7H_2$)	5.1×10^{-4}	0.020	2.1×10^{-4}	0.012	2.0×10^{-6}	4.8×10^{-4}
η ($C_2H_4 \rightarrow {}^1/_3C_6H_6 + H_2$)	0.40	1.0	0.21	0.76	2.4×10^{-3}	0.025
η ($C_2H_4 \rightarrow {}^2/_7C_7H_8 + {}^6/_7H_2$)	0.061	0.26	0.028	0.14	2.5×10^{-3}	0.020

(673 K; Figure 2), but maximum selectivities are lower (~55%) and occur at lower conversions (30%).

An indication of the extent to which various reactions are limited by equilibrium can be obtained from the approach to equilibrium data shown in Table 2. Propane conversion to benzene is far from equilibrium at all conversions, suggesting that net benzene formation rates are largely unaffected by its reverse reaction. Propene to benzene and propane to toluene conversions are also far from equilibrium. Other reactions, such as ethene conversion to benzene, are near equilibrium at high propane conversions (>60%) on Ga/H-ZSM5. The approaches to equilibrium for ethene to toluene reactions are smaller than those for ethene conversion to benzene (0.26 vs 1.0, at 80.8% conversion; Ga/H-ZSM5), but reverse reactions cannot be neglected, even for the former reaction. Thus, some ethene formed in primary propane cracking steps cannot convert to aromatics because of thermodynamic constraints; instead, they hydrogenate to form unreactive ethane molecules as H_2 pressures increase with increasing conversion.[26] The net rate for all reactions with nonzero η values will increase as H_2 is removed in combustion reactions favored by thermodynamics.

The presence of H_2 during propane reactions leads to a shift in selectivity toward hydrogen-rich cracking products and to a decrease in dehydrogenation and aromatization rates on Zn/H-ZSM5[18] and Co/H-ZSM5.[26] These effects of H_2 are much stronger on cation-exchanged H-ZSM5 than on H-ZSM5 because cations activate H_2 and introduce hydrogen into the surface pool of reactive intermediates. At low propane conversions, Ga and Zn remove hydrogen from this pool as H_2, but as alkane conversion and H_2 concentrations increase, the reverse of this reaction leads to dissociative adsorption and to unfavorable thermodynamics for required surface reactions. In effect, as one or more of the required dehydrogenation steps approach equilibrium, H_2 leads to lower net reaction rates because the rate of the corresponding reverse reactions gradually increases. In contrast, the rate of cracking reactions that form CH_4 and of C_2H_4 hydrogenation to form C_2H_6 are either unaffected by H_2 or increase with increasing H_2 pressure because these reactions remain far from equilibrium at all propane conversion levels.

Effects of Hydrogen Removal by Staged O_2 Introduction on C_3H_8 Reactions. Selective stoichiometric reactions of H_2 during propane reactions can remove these kinetic and thermodynamic barriers. The reported beneficial effects of O_2 on aromatics selectivity combined with the observed undesired hydrocarbon combustion reactions[5,8] led us to explore the staging of O_2 co-reactants so as to match the rate at which H_2 becomes available from C_3H_8 reactions. The effects of O_2 staging were examined using a gradientless batch reactor that rigorously simulates the gradual injection of O_2 via multiple injectors or oxygen-permeable walls in plug-flow reactors. O_2 introduction rates were initially chosen based on average H_2 formation rates (staging intensity of unity) and then varied around these stoichiometric values.

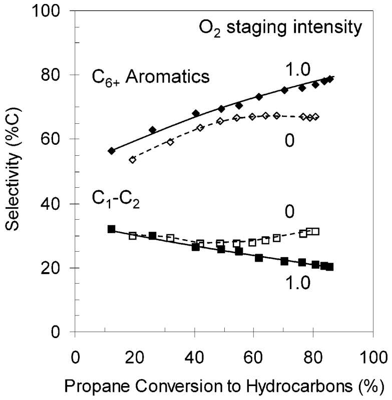


Figure 3. Effects of oxygen staging on product selectivities on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) in gradientless batch reactors [773 K, 20 kPa propane, 3.3 mmol/g-atom of Al s O_2, balance He].

At low conversions (<60%), staged O_2 introduction did not significantly influence propane conversion rates and selectivities on 1.8 wt % Ga/H-ZSM5 (Figure 3), but led to higher rates and selectivities at higher C_3H_8 conversions. The highest achievable C_{6+} aromatics selectivity was significantly higher (~80%) and was reached at higher conversions (85%) than with pure C_3H_8 reactants (67% at ~70% conversions). The maximum attainable yields of C_{6+} aromatics increased from 54% for C_3H_8 reactants to 68% with stoichiometric O_2 staging on Ga/H-ZSM5. Such C_{6+} aromatics yields are much higher than those previously reported for propane reactions on Ga/H-ZSM5 or Zn/H-ZSM5.[3,19] Cracking selectivities were significantly lower with staged O_2 injection than with pure C_3H_8 reactants, especially at high conversions (Figure 3). C_3H_6 and C_4-C_5 selectivities were less affected by O_2 addition and H_2 removal than cracking selectivities (Table 1). O_2 co-reactants decreased C_3H_6 (3.5% to 2.9%) and C_4-C_5 (1.4% to 0.8%) selectivities at 60% conversion on Ga/H-ZSM5. C_3H_6 and C_4-C_5 products ultimately convert to C_{6+} aromatics; thus, a rigorous measure of reactant efficiency is given by the ratio of desired aromatic products to undesired cracking products, especially unreactive ethane and methane. Figure 4 shows that O_2 addition strategies lead to almost a 2-fold increase in this ratio at the high C_3H_8 conversion levels required for practical C_{6+} aromatic yields.

Propane reaction pathways include primary dehydrogenation steps that form C_3H_6 and primary cracking steps that form CH_4 and C_2H_4 directly from propane, as shown in Scheme 1.[26] Secondary products include C_2H_6 and C_{6+} aromatics.[26] O_2 addition did not strongly

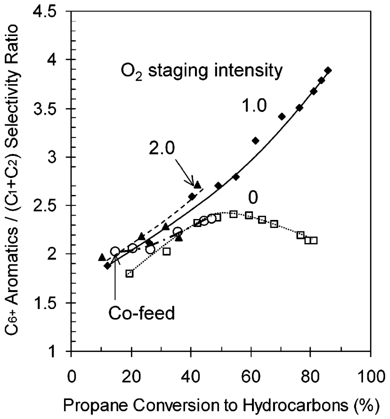


Figure 4. C_{6+} aromatics to $C_1 + C_2$ selectivity ratio versus propane to hydrocarbons conversions [773 K, 20 kPa Propane, 13 kPa O_2 (co-feed), 3.3, 6.6 mmol/g-atom of Al s O_2, balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25)].

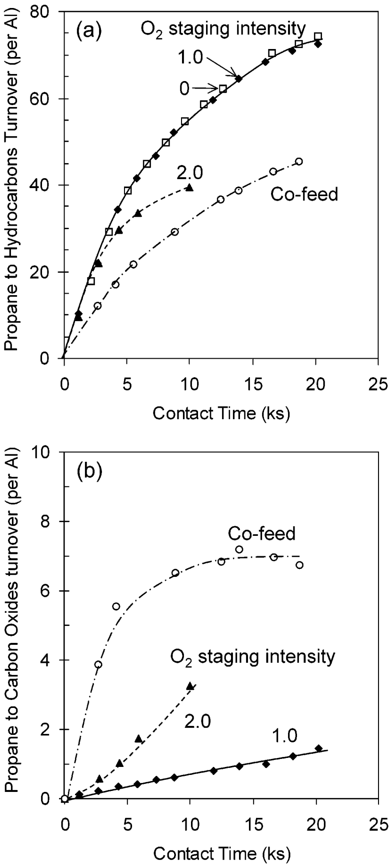


Figure 5. Propane to (a) hydrocarbons turnovers and (b) carbon oxides turnovers during propane dehydrocyclodimerization on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) [773 K, 20 kPa propane, 13 kPa O_2 (co-feed), 3.3, 6.6 mmol/g-atom of Al s O_2, balance He].

influence C_3H_8 conversion rates (Figure 5a), consistent with the fact that primary reactions are far from equilibrium (Table 2) and thus unaffected by H_2 removal. O_2 co-reactants decreased C_2 site yields (Figure 6b), especially as conversion increased with increasing contact time, but did not affect CH_4 formation rates (Figure 6a). In all cases, the C_2/C_1 molar ratio was smaller than 2, the value expected from primary cracking steps (Table 3, Scheme 1). Thus, primary cracking rates were not affected by H_2 concentration or by its removal with O_2, but the latter influenced the relative rates of C_2H_4 hydrogenation and aromatization reactions. Indeed, the near-equilibrated nature of ethene conversion to aromatics prevents the net incorporation of C_2H_4 into the aromatics pool, while the high prevalent H_2 concentrations with pure C_3H_8 reactants favors its hydrogenation to form unreactive C_2H_6. Thus, O_2 addition shifts the equilibrium for ethene conversion to aromatics, while concurrently removing the H_2 co-reactants required for parallel undesired hydrogenation steps.

The efficiency of O_2 co-reactants in removing H_2 is given by the percentage of the converted O_2 that forms

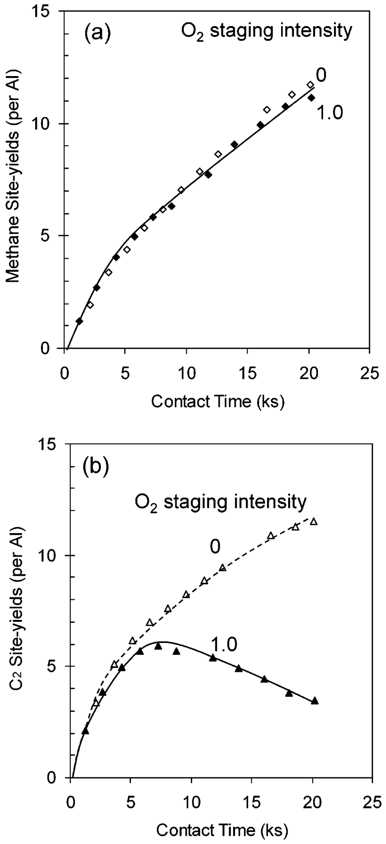
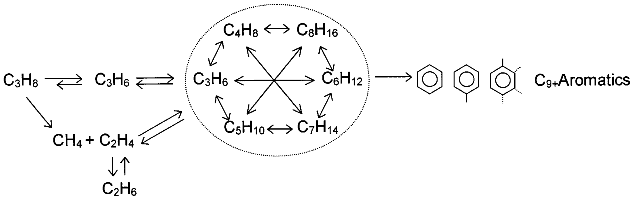


Figure 6. (a) Methane and (b) C_2 (the sum of ethene and ethane) site yields during propane dehydrocyclodimerization on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) [773 K, 20 kPa propane, 3.3 mmol/g-atom of Al s O_2, balance He].

Table 3. Effects of Oxygen Staging on the Ratios of C_2 to C_1 Site Yields on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) in Gradientless Batch Reactors [773 K, 20 kPa Propane, 3.3 mmol/g-atom of Al s O_2, Balance He]

C_3H_8		C_3H_8/staged O_2	
propane conversion %	C_2/C_1 site yields ratio	propane conversion %	C_2/C_1 site yields ratio
31.8	1.52	25.9	1.43
59.5	1.17	61.6	0.90
80.8	1.00	80.8	0.48

Scheme 1. Reaction Pathways for Propane Conversion on ZSM5-Based Catalysts. Adapted from Ref 26



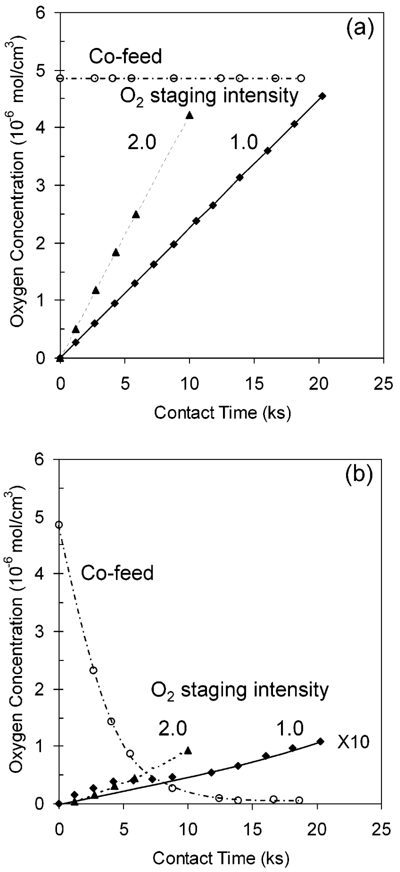


Figure 7. (a) Total amounts of introduced oxygen and (b) residual oxygen during propane dehydrocyclodimerization on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) [773 K, 20 kPa propane, 13 kPa O_2 (co-feed), 3.3, 6.6 mmol/g-atom of Al s O_2, balance He].

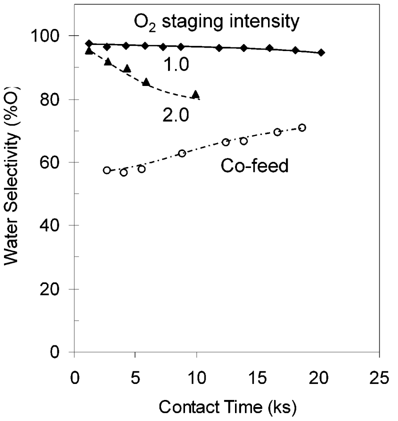


Figure 8. H_2O selectivity (%O base) during propane dehydrocyclodimerization on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) in recirculating batch reactors [773 K, 20 kPa propane, 13 kPa O_2 (co-feed), 3.3, 6.6 mmol/g-atom of Al s O_2, balance He].

H_2O instead of CO_x (CO and CO_2). Figure 7 shows the added and residual O_2 amounts for a staging intensity of unity on Ga/H-ZSM5. Residual O_2 concentrations are very low (<0.11 μmol/cm^3) throughout the entire range of conversion and contact time. Figure 8 shows that H_2O selectivities for this staging intensity are 95−98%, indicating that H_2 removal by O_2 is remarkably selective, as long as H_2 is present to deplete O_2 co-reactants. H_2O selectivities decreased slightly with increasing conversion, apparently because reaction products are more reactive than C_3H_8 in combustion reactions and these products may also inhibit homogeneous H_2 combustion rates via radical trapping.[27] In addition, the decrease in H_2 formation rates with increasing C_3H_8 conversion leads to the ultimate accumulation of some unreacted O_2 and to its greater involvement in hydrocarbon oxidation.

Staged O_2 addition strategies lead to similar selectivity and yield improvements on Zn/H-ZSM5 and H-ZSM5 (Table 1) and these results are discussed in a later section.

Effects of O_2 Staging and Co-feed Strategies on Ga/H-ZSM5. In view of the marked improvements in hydrocarbon and O_2 selectivities achieved by stoichiometric staging of O_2 co-reactants, we examined the effects of staging intensity on reaction rates and selectivity. Experiments were carried out using 20 kPa C_3H_8 by either introducing O_2 initially with propane reactants (13.4 kPa) or using an O_2 staging intensity of 1.0 (3.3 mmol/g-atom of Al s). These data were compared with those obtained in co-feed mode, in which the amount of O_2 added over 20 ks during staged experiments was added initially together with C_3H_8 reactants. Residual O_2 concentrations are initially very high in this co-feed mode, but they decreased rapidly as O_2 is predominately consumed in fast hydrocarbon combustion reactions (Figure 7b). O_2 concentrations become undetectable at contact times required for ~35% propane conversion. In the absence of significant H_2 concentration, reactions of O_2 are fast and unselective and O_2 remains available only for contact times leading to relatively low C_3H_8 conversions, for which H_2 removal has minor kinetic and thermodynamic consequences. O_2 is available continuously and present at much lower average concentrations when it is introduced continuously as propane reacts and H_2 is formed.

The depletion of O_2 at ~35% C_3H_8 conversions causes subsequent propane reactions to occur without the benefit of H_2 removal; yet, it is precisely at higher conversions that rates and selectivities would benefit from selective H_2 reactions with O_2 (Figure 4). At low conversions, co-feed and staging O_2 strategies lead to similar effects on aromatic/cracking selectivity ratios, but these effects disappear as O_2 is depleted via unselective reactions in the co-feed mode, while they continue at higher conversion because of the continuous availability of O_2 during staged O_2 operation (Figure 4).

The high initial O_2 concentrations prevalent in co-feed operating modes lead to the unselective use of O_2 in combustion of propane and of its reaction products (Figures 5b and 8). Figure 5b shows CO_x formation turnovers for co-feed and stoichiometric staging cases. CO_x formation rates are initially very high in co-feed mode, but decrease with contact time as O_2 is depleted. CO_x formation rates are much lower at the lower O_2 concentrations prevalent during staged O_2 introduction. More importantly, the selectivity for O_2 consumption in H_2O formation is very low in the co-feed mode (Figure 8) because O_2 concentrations are highest during the early reaction stages, when H_2 is unavailable (Figure 7b). O_2 concentrations decrease rapidly to undetectable levels as H_2 becomes available with increasing C_3H_8 conversion. O_2 is used selectively to form H_2O during stoichiometric O_2 staging (Figure 8) and H_2O selectivities remain above 95% at all conversion levels. In contrast, initial H_2O selectivities are very low (~57%) in the co-feed mode and increase to ~70% as O_2 is depleted with increasing contact time (Figure 8). Thus, staging strategies provide an attractive route for the

Table 4. Propane to Carbon Oxides Turnover Rates on 1.8% Ga/H-ZSM5 and with Empty Reactor [Catalytic Reactions: 773 K, 20 kPa Propane, 2.2 mmol/g-atom of Al s O_2, Balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25), Homogeneous Reactions: 773 K, Reactants and Products after the Catalytic Reaction for 7.2 ks, at the Same O_2 Rate as with Catalyst, Empty Reactor]

	Ga/H−ZSM5		homogeneous		
contact time (ks)	5.7	7.2	2.1	5.1	11.1
carbon oxides formation rate (mol/cm^3 (heated volume), 10^{-9} s^{-1})	9.2	8.8	8.8	8.8	28.3
H_2 combustion rate (mol/cm^3 (heated volume), 10^{-7} s^{-1})	1.2	1.2	1.1	1.1	–
residual H_2 concentration (mol/cm^3 (reactor volume), 10^{-6})	3.6	3.0	1.7	0.71	0.00
residual O_2 concentration (mol/cm^3 (reactor volume), 10^{-8})	3.4	3.5	3.6	4.1	92.9

selective use of O_2 in propane dehydrocyclodimerization reactions and lead to much higher aromatics selectivities and O_2 reactant efficiencies than co-feed operating modes.

To determine the extent to which homogeneous pathways contribute to CO_x formation, reaction products and unreacted C_3H_8 were isolated after reaction (to 55% conversion) on Ga/H-ZSM5 for 7.2 ks at 773 K using an O_2 staging intensity of 0.67 (2.2 mmol/g-atom of Al s). This mixture was then reacted in an empty reactor (2.0-cm^3 heated volume) identical to that used in catalytic experiments, while O_2 introduction was continued at the same molar rate. The results of this experiment are shown in Table 4. CO_x formation and H_2 combustion rates were initially unchanged by the removal of Ga/H-ZSM5 catalyst, indicating that homogeneous oxidation pathways are sufficiently rapid to account for all the CO_x formed and all of H_2 combusted during O_2 staging. As H_2 was depleted by continuous O_2 addition, CO_x formation rates increased markedly because of the resulting increase in O_2 concentrations. We conclude that tubular packed bed reactors, with void to catalyst volume ratios of ~1 are likely to give even lower CO_x selectivities than measured in our reactors, for which this volume ratio is ~20.

Effect of O_2 Introduction Rates on Propane Reaction on Ga/H-ZSM5. We have also examined the effects of O_2 staging intensity (0, 0.67, 1.0, 1.5, and 2.0) on hydrocarbon and oxygen selectivities for propane reactions on Ga/H-ZSM5. At an O_2 staging intensity of 2.0, O_2 concentrations increased gradually with time (Figure 7b) because H_2 formed in dehydrogenation reactions is quickly depleted (Figure 9) and the residual O_2 reacts only in slower hydrocarbon oxidation reactions. Staging intensities above stoichiometric values lead only to small additional improvements in aromatics/cracking selectivity ratios over those achieved with stoichiometric staging (Figure 4); they lead, however, to lower O_2 reactant efficiencies and H_2O selectivities (Figure 8). CO_x turnover rates increased markedly as staging intensities reached values above 1 (Figure 5b). The stoichiometric case provides the amount of O_2 required for H_2 depletion and avoids the presence of residual O_2 for slower competitive reactions with hydrocarbons. Aromatics/cracking selectivity ratios and H_2O selectivities are shown at 40% propane conversion as a function of O_2 staging intensity in Figure 10. O_2 staging intensity strongly influenced selectivities for values less than 1, but only weakly at higher staging intensities. Aromatics selectivities increased monotonically with staging intensity, while H_2O selectivities decreased sharply above stoichiometric values.

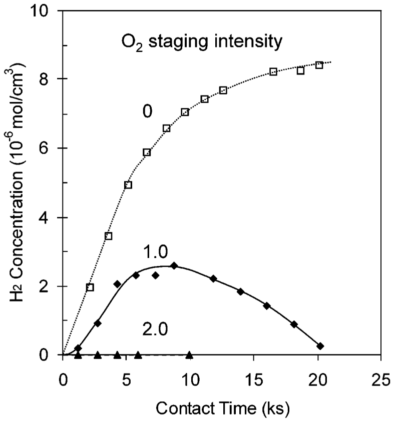


Figure 9. Effects of O_2 staging intensity on hydrogen concentration during propane dehydrocyclodimerization on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) [773 K, 20 kPa propane, 3.3, 6.6 mmol/g-atom of Al s O_2, balance He].

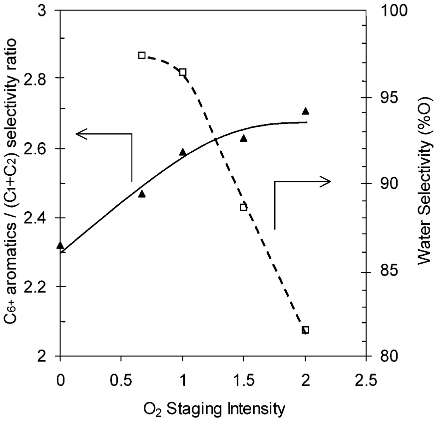


Figure 10. Effects of O_2 staging intensity on C_{6+} aromatics to C_1 + C_2 selectivity ratio and H_2O selectivity (%O base) on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) in a recirculating batch reactor [773 K, 20 kPa propane, 2.2−6.6 mmol/g-atom of Al s O_2, balance He, 39−42% propane conversion].

Interestingly, staging intensities above 1 also lead to lower propane dehydrocyclodimerization rates on Ga/H-ZSM5 (Figure 5a). This loss of activity may reflect (1) oxidation of active sites by the excess O_2, (2) loss of zeolite crystallinity or accessibility caused by higher H_2O concentrations, or (3) deposition of unreactive organic residues at the low prevalent H_2 concentrations. Indeed, exchanged Ga^+ species may oxidize to GaO^+,[10] but Zn/H-ZSM5, in which Zn cations remain divalent throughout treatments in H_2, propane, and O_2, showed similar losses in activity at high O_2 introduction rates. Thus, we conclude that oxidation is not responsible for the observed loss of catalytic activity. Treatment in flowing dry air at 773 K for 2 h restored 95% of the initial propane conversion rates, suggesting that loss of crystallinity is not responsible for the observed deactivation.

Unsaturated organic residues are favored by the low H_2 levels prevalent at high O_2 introduction rates, especially when these low H_2 levels coexist with significant concentrations of unsaturated molecules formed in propane reactions.[18] It is expected that such residues would be favored at conditions that also lead to high aromatics selectivity, as these residues form from unsaturated adsorbed intermediates. These conclusions are consistent with the observed increase in the size of aromatic products with increasing staging intensity

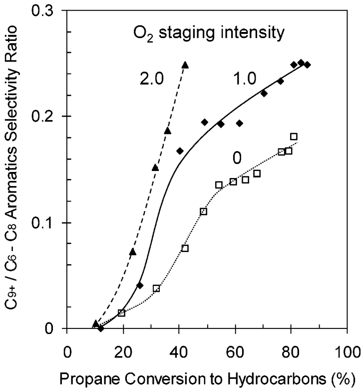


Figure 11. Effects of O_2 staging intensity on $C_{9+}/C_6 - C_8$ aromatics selectivity ratio on 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25) in recirculating batch reactors [773 K, 20 kPa propane, 3.3 (stoichiometric staging), 6.6 (excess staging) mmol/g-atom of Al s O_2, balance He].

(Figure 11). In addition, the presence of ^{13}CO in $^{12}C_3H_8$ reactants led to catalytic deactivation and to the formation of labeled carbon deposits;[8] thus, the higher CO_x concentrations present at above stoichiometric staging intensities may also lead to deactivating deposits.

We conclude that the benefits of selective H_2 removal with O_2 depend on some critical variables: the time (or reactor position) and the rate at which O_2 is introduced, the presence of O_2 only as H_2 becomes available from dehydrogenation reaction, and the retention of some H_2 to moderate the tendency of active sites to form large and highly unsaturated products and adsorbed intermediates. A balance among these variables is achieved when the intensity and location (or time) of O_2 introduction is controlled so as to maintain a low but nonzero concentration of H_2 throughout the reactor. This balance is typically achieved at staging intensities slightly below stoichiometric and when introduction rates can be adjusted to reflect changes in propane dehydrocyclodimerization rates as the kinetic driving force decreases along the reactor (in a tubular flow reactor) or with increasing contact time (in a semibatch reactor).

Effects of O_2 Staging on Propane Dehydrocyclodimerization Reactions Catalyzied by H-ZSM5 and Zn/H-ZSM5. Here, we examine the effects of stoichiometric O_2 staging during propane reactions on H-ZSM5 and 1.0% Zn/H-ZSM5 and compare them with those described above for 1.8% Ga/H-ZSM5. Some of the relevant results are shown in Figure 12a–c and in Table 1. In each case, the staging intensity is defined as the ratio of the total amount of introduced O_2 to that required to consume all H_2 formed during alkane reactions. O_2 staging led to a significant increase in aromatics/cracking selectivity ratios on all three catalysts (Figure 12a). These effects are stronger when cations are present in H-ZSM5 because dehydrogenation reactions, and specifically ethene conversion to aromatics, a reaction that preserves ethene within the reactive alkene pool, are much closer to equilibrium than on H-ZSM5 (Table 2). The principal role of H_2, and the main benefit of its removal via selective combustion, is to shift the equilibrium of this reaction toward the formation of aromatics and the reaction selectivity away from the formation of less reactive ethane (Scheme 1). At these staging intensities, propane conversion rates are essentially unaffected by O_2 introduction (Figure 12b), suggesting that only the relative rates of secondary reactions, and not primary dehydrogenation and cracking reactions of propane, depend on H_2 concentration. On all three catalysts, benzene and C_{9+} aromatics selectivities were significantly higher with O_2 coreactants than with pure C_3H_8 (Table 1), while selectivities to toluene and xylenes were less sensitive to O_2 staging. This appears to reflect the closer approach to equilibrium for ethene conversion to benzene relative to those for ethene conversion to toluene and xylenes (Table 2).

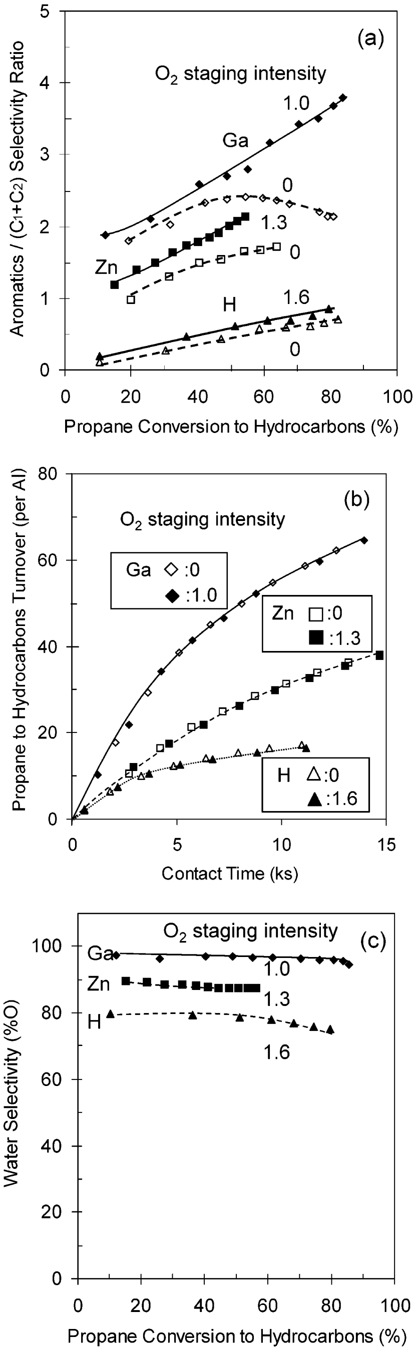


Figure 12. Effects of oxygen staging on (a) C_{6+} aromatics to $C_1 + C_2$ selectivity ratios; (b) propane to hydrocarbons turnovers; (c) H_2O selectivities (%O base): Without oxygen (open marks), with staged oxygen (closed marks) [773 K, 20 kPa propane, 3.3 (Ga), 1.7 (Zn), 0.75 (H) mmol/g-atom of Al s O_2, balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25); 1.0 wt % Zn/H-ZSM5 (Zn/Al = 0.14); H-ZSM5 (Si/Al = 14.5)].

Figure 12 shows selectivities for O_2 conversion to H_2O at different staging intensities on each catalyst. At similar O_2 staging intensities (1.3), H_2O selectivities are

Table 5. Relative Combustion Rates of Hydrocarbons during Homogeneous Reaction [Homogeneous Reaction: 773 K, Reactants and Products after the Catalytic Reaction for 7.2 ks, at the Same O_2 Rate as with Catalyst, Empty Reactor; Catalytic Reaction: 773 K, 20 kPa Propane, 2.2 mmol/g-atom of Al s O_2, Balance He, 1.8 wt % Ga/H-ZSM5 (Ga/Al = 0.25)]

	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_{6+} aromatics
relative combustion rates	0.017	1.6	0.13	12	1.0	1.8

similar on Zn/H-ZSM5 (89%) and Ga/H-ZSM5 (91%). At higher values of staging intensity (1.6), H_2O selectivities were lower on H-ZSM5 (79%) than on Ga/H-ZSM5 (87%). Propene selectivities are higher and H_2 selectivities lower on H-ZSM5 than on Ga or Zn/H-ZSM5 (Table 1) at all conversion levels. The homogeneous oxidation first-order rate constant for propene is much higher (12.6 relative to propane) than those for propane (1.0) and aromatics (1.8). These values were obtained from disappearance rates for each hydrocarbon during homogeneous reaction experiments (Table 5). The more reactive nature of the products formed and their relatively high abundance compared with H_2 appear to account for the lower H_2O selectivities measured on H-ZSM5 relative to those on cation-exchanged H-ZSM5.

Conclusions

Semibatch reactors with continuous O_2 introduction were used to probe the effects of selective H_2 combustion during propane dehydrocyclodimerization reactions on H-ZSM5, Zn/H-ZSM5, and Ga/H-ZSM5. These experiments rigorously simulate the gradual injection of O_2 along a plug-flow reactor via mutiple injectors or oxygen-permeable walls. Controlled O_2 introduction strategies led to selective combustion of the H_2 formed during propane reactions. This approach overcomes the kinetic and thermodynamic inhibition effects of H_2, which limit aromatic yields in these reactions. Specifically, selective H_2 removal increases the net rate of the nearly equilibrated conversion of the ethene formed in cracking reactions into aromatics. It also decreases the rate at which ethene converts to unreactive ethane. These O_2 staging protocols provide an attractive route for the selective use of O_2 for H_2 combustion (H_2O selectivity >95%), which appear to proceed via homogeneous pathways. Staging intensities near unity (stoichiometric addition case) led to a 2-fold increase in the aromatization to cracking selectivity ratio and to unprecedented aromatics yields (~70%) on Ga/H-ZSM5, even at relatively low temperature (773 K). The introduction of an equivalent amount of O_2 with propane reactants led to the unselective depletion of O_2 in hydrocarbon oxidation reactions and to the substantial absence of O_2 as H_2 is formed in propane dehydrocyclodimerization reactions. These benefits of O_2 introduction were also detected on Zn/H-ZSM5 and H-ZSM5 catalysts. On H-ZSM5, the higher selectivity to propene products, which are much more reactive than propane or aromatics in homogeneous oxidation reactions, and the lower H_2 selectivity led to less selective use of added O_2 in H_2 removal reactions.

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