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Mechanism of intra- and inter-molecular C=C bond formation of propanal on Brønsted acid sites contained within MFI zeolites

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ABSTRACT

Kinetic and chemical titration studies are used to unravel the reaction pathways and catalytic requirements for propanal deoxygenation over Brønsted acid sites contained within MFI zeolites. Propanal deoxygenation in the absence of external hydrogen source is initiated via primary and competitive pathways of inter- and intra-molecular C=C bond formation that involve bimolecular coupling of propanal and uni-molecular deoxygenation steps, respectively. The inter-molecular C=C bond formation proceeds via mechanistic steps resembled the acid-catalyzed aldol condensation reactions in the homogeneous phase, and its reactive collision frequencies increase with increasing propanal pressure. The reaction is initiated by keto–enol tautomerization of propanal to form small concentrations of propenol. The propenol undergoes kinetically-relevant nucleophilic attack to protonated propanal, the most abundant surface intermediates, to create the inter-molecular C=C bond. The competitive uni-molecular deoxygenation step involves kinetically-relevant hydrogen transfer from hydrogen-donating agents and occurs at rates that remain invariance with propanal pressure. Hydrogen-donating agents are aliphatic rings produced from consecutive inter-molecular C=C bond formation and ring closure events and donate hydrogen via dehydrogenation steps to increase their extent of unsaturation. Hydrogen-donating events must kinetically couple with the direct hydrogen insertion step on propanal to satisfy the deoxygenation stoichiometry and form propanol, which upon dehydration evolves predominantly propene, thus preserving the carbon backbone. Water as a by-product prevents binding of larger, inactive carbonaceous species on acid sites and inhibits the inter-molecular C=C bond formation step by increasing the reverse rate of this step. Water, however, does not alter the net rate for intra-molecular C=C bond formation, because of its irreversible nature. An increase in the rate ratio for intra- over inter-molecular C=C bond formation upon the addition of 3-methyl-1-pentene, an effective hydrogen-donating agent, confirms the kinetic relevance of the hydrogen transfer step for propene formation. These findings on the different kinetic dependencies for the competitive reactions and their mechanistic interpretations provide the operating strategies to tune the reaction pathways, manipulate the extent of hydrogen transfer, and tailor the distributions of larger oxygenates and alkenes during propanal deoxygenation reactions.

1. Introduction

Small oxygenates of alkanal and alkanone (R–CHO, RC(=O)R′; R ⩽ 4) produced from biomass pyrolysis could be catalytically upgraded to value-added chemicals, hydrocarbons, or aromatics [1–3] by reactions that remove oxygen heteroatoms and lengthen their carbon backbone. The aldol-type condensation reactions couple alkanal (R–CHO) or alkanone (RC(=O)R′) reactants to increase their carbon chain length and eject an oxygen atom as H_2O without the use of external H_2 [2,4,5]. The condensation reactions may occur in acidic and basic medium and, in the homogenous phase, mechanistic pathways and catalytic functions of acid and base have been well established [6]. The acid-catalyzed C–C bond formation [6–8] occurs via an initial keto–enol tautomerization of alkanal (or alkanone) to form the conjugate enol. The sequential nucleophilic attack of the alpha carbon in enol to the protonated carbonyl group of alkanal (or alkanone) creates an inter-molecular C–C bond, thus lengthening the carbon backbone and forming a beta-hydroxy alkanal (or alkanone), also known as an aldol. The base-catalyzed C–C bond formation [6] involves the formation of a resonance-stabilized enolate and its sequential nucleophilic attack to the carbonyl group of an alkanal or alkanone to evolve the aldol. Both acid- and base-catalyzed reactions share a common sequential dehydration step that transforms the beta-hydroxyl alkanal (or alkanone) to an alkenal or alkenone, respectively, to complete a catalytic turnover [6].

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Similar reactions have been reported on acid sites [9–11], basic sites [12,13], or bifunctional acid–basic site pairs [14–17] immobilized within solid structures. Condensation reactions on solid basic sites (e.g., on Mg–Al mixed oxide) form almost exclusively the expected primary condensation products at low temperatures (353–413 K) [12,13]. Mg–Al mixed oxides catalyze heptanal and benzaldehyde reactions to form a mixture of cross-condensation (jasminaldehyde) and self-condensation (2-*n*-pentyl-2-nonenal) products at selectivities of 67–80% and 20–33%, respectively, at 403 K [12,13]. Alkali ion-exchanged zeolites (Na–X, K–X, and Cs–X), alkali-treated alumina (KOH–Al_2O_3), and hydrotalcite {$[Mg_{0.6}Al_{0.4}(OH)_2](CO_3)_{0.20}\cdot 0.84H_2O$} convert propanal to 2-methyl-2-pentenal and 3-hydroxyl-2-methylpentanal (373 K) [12]. Similarly, alkaline earth metal oxides (e.g., MgO and SrO) promote butanal condensation to form predominantly the self-condensation product (2-ethyl-2-hexenal) at carbon selectivities above 90% with a small amount of 2-ethyl-2-hexenol, heptanone, and 2-ethylhexanol at 573 K [14]. As the temperature increases, ketonization, reverse α-addition, cracking, and decarboxylation reactions begin to occur on basic sites (e.g., on MgO/SiO_2 [14], SrO/SiO_2 [14], and $Ce_xZr_{1-x}O_2$ [18]) at detectable rates relative to those of primary condensation reactions, as reported for propanal reactions on MgO/SiO_2 and SrO/SiO_2 (>723 K) [14] and butanal reactions on $Ce_xZr_{1-x}O_2$ (>673 K) [18].

On Brønsted acid catalysts (H-MFI) [4,5,19], the initial coupling of alkanals leads to larger oxygenates, which undergo secondary reactions of aromatization, alkylation/dealkylation, and cracking. At higher temperatures (e.g., 673 K), these secondary reactions occur much faster than the initial alkanal turnovers and lead to diverse methyl- or ethyl-substituted aromatics (e.g., trimethylbenzene, methyl-ethylbenzene) and light gases (e.g., CO, CO_2, C_1–C_3 hydrocarbons). The primary condensation products were detected on H-MFI at these higher temperatures only when introducing alkanal reactant in pulses to maintain the pressures of alkanal and primary products at low values [4].

Condensation, aromatization, and cracking reactions during alkanal conversions on Brønsted acid sites (H^+) contained within microporous crystalline silica–alumina frameworks have been recently proposed to involve pools of oxygenate and hydrocarbon intermediates coexisted within the zeolitic pores [4]. The primary and secondary nature of these reactions, rate dependencies of individual catalytic paths, identity of kinetically-relevant steps, and associated mechanistic details have not been rigorously established. The lack of such molecular level details is caused, in large part, by the complexity of the reaction network. The mechanistic knowledge, kinetic dependencies, and site requirements for the C–C bond formation and oxygen removal are, however, crucial for predicting and tailoring the product distributions and their yields.

Herein, we interrogate the fate of propanal during their catalytic sojourns over Brønsted acid sites (H^+) contained within MFI framework. We propose a sequence of elementary reactions to describe the fate of propanal in competitive reactions that create an inter- and intra-molecular C=C bond to evolve 2-methyl-2-pentenal and propene, respectively. We also discuss secondary reactions of ring closure, dehydration, and dehydrogenation that evolve the larger aromatics and requirements of hydrogen transfer between the secondary dehydrogenation step and the intra-molecular C=C bond formation step to satisfy the reaction stoichiometry. We draw a mechanistic synergy between the reactions occurring at acid sites contained within the microporous crystalline materials and those in the homogeneous phase and then report a competitive direct deoxygenation path undetected in homogeneous reactions. The rate dependencies for these reactions were measured, their kinetic relevance and reversibility were interrogated, and the kinetic couplings of hydrogen transfer within the catalytic sequence were confirmed.

2. Experimental

2.1. Catalyst synthesis

MFI zeolite samples in their NH_4^+ form (425 $m^2\,g^{-1}$, Si/Al atomic ratio = 11.5, CBV2314, Zeolyst) were treated in flowing dry air (0.6 $cm^3\,g^{-1}\,s^{-1}$, zero grade, Linde) to 873 K by increasing the temperature at 0.0167 K s^{-1} and holding for 4 h to convert NH_4^+ to H^+. In a separate series of MFI zeolite samples, ion exchange was performed to exchange the NH_4^+ ions with Na^+ ions to attain final samples with varying H^+ and Na^+ contents (atomic ratios of $H^+/Al = 0.82–0.48$ and $Na^+/Al = 0–0.34$). NH_4^+-MFI zeolites (Si/Al = 11.5, 4 g) were mixed and stirred with aqueous NaCl solution {7.8–70 g of NaCl (99%, ACP Chemicals) and 100 cm^3 of doubly deionized water} at 298 K for 24 h. The samples were then washed in doubly deionized water and filtered under vacuum until Cl^- ions in the filtrate were undetected from chemical titration with 0.1 mol L^{-1} $AgNO_3$ (99.9999%, Sigma Aldrich) aqueous solution. The samples were dried at 393 K for at least 8 h and then heated in flowing dry air (0.6 $cm^3\,g^{-1}\,s^{-1}$, zero grade, Linde) at 0.0167 K s^{-1} to 873 K and holding for 4 h at 873 K to convert NH_4^+ to H^+.

2.2. Catalytic rates and selectivities of propanal and 1-propanol reactions on MFI zeolites

Chemical turnover rates and selectivities of propanal reactions were measured in a fixed bed tubular microcatalytic quartz reactor (inner diameter of 9.5 mm) with plug-flow hydrodynamics and operated under continuous flow mode. The reactor was contained within a resistively heated furnace with its temperature regulated using a digital feedback temperature controller. Catalyst samples (300 mg) were supported on a quartz frit and the reaction temperature was recorded using a K-type thermocouple placed at the center of the axial and radial directions of the catalyst bed.

Catalysts were heated in flowing He (2.8 $cm^3\,g^{-1}\,s^{-1}$, Grade 5.0, Linde) at 0.0167 K s^{-1} to reaction temperatures (473–673 K) prior to rate measurements. Propanal (Kosher grade, ⩾97%, Sigma Aldrich) was used as received and introduced via a gas tight syringe (Model 008025, 1 cm^3, SGE) mounted on a syringe infusion pump (Model LEGATO 100, KD Scientific) into a vaporizing zone, in which it was evaporated and mixed with a He purge stream (0.83 $cm^3\,s^{-1}$, Grade 5.0, Linde) at 320 K. All gas lines for transferring reactant mixtures were heated to 320 K and product mixtures were heated to 473 K to prevent condensation. Reactions of 1-propanol (⩾99.9%, Sigma Aldrich) on H-MFI were carried out following the same procedure with 0.58 kPa 1-propanol and at a space velocity of 6×10^{-4} mol 1-propanol (mol H_i^+ s$)^{-1}$.

Reactions using propanal and water (C_3H_6O–H_2O) or propanal and 3-methyl-1-pentene (C_3H_6O–C_6H_{12}) feed mixtures were carried out by introducing either doubly deionized H_2O or 3-methyl-1-pentene (99%, Sigma Aldrich) into a second vaporizing zone maintained at 363 K or 330 K, respectively, located downstream from the vaporizer used for propanal evaporation (described above). Doubly deionized H_2O or 3-methyl-1-pentene was introduced via a gas tight syringe {Model 1005, 5 cm^3 (Hamilton) for H_2O and Model 006230, 0.25 cm^3 (SGE) for C_6H_{12} infusion} mounted on a syringe infusion pump (Model KDS-100, KD Scientific, for H_2O or Model LEGATO 100, KD Scientific, for C_6H_{12} infusion).

Chemical species in the feed and reactor effluent stream were quantified using an online gas chromatograph (Model 7890A, Agilent) and mass spectrometer (Model 5975C, Agilent), GC–MS, equipped with a 10-port sampling valve containing two sample loops of 250 μL each. The samples contained in the gas sampling