



Alkanal transfer hydrogenation catalyzed by solid Brønsted acid sites



Fan Lin, Ya-Huei (Cathy) Chin*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto M5S 3E5, Canada

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ABSTRACT

Catalytic pathway and requirements for transfer hydrogenation of *n*-alkanals ($C_nH_{2n}O$, $n = 3-6$) on Brønsted acid sites (H^+) immobilized in microporous MFI and FAU crystalline structures or dispersed on $H_4SiW_{12}O_{40}$ polyoxometalate clusters are established by isolating its rates from those of the various concomitant catalytic cycles. Transfer hydrogenation of alkanals involves a kinetically-relevant, inter-molecular hydride transfer step from substituted tetralins or cyclohexadienes produced from the parallel alkanal coupling and ring closure reactions as the hydride donor ($R'H_2$) to protonated alkanals (RCH_2CHOH^+) as the hydride acceptor, via a bi-molecular transition state with a shared hydride ion, ($RCH_2CHOH^+ \cdots H^- \cdots R'H^+$)[‡]. The rate constants for the inter-molecular hydride transfer step correlate directly to the hydride ion affinity difference between the carbenium ions of the H-donors ($R'H^+$) and the protonated alkanals (RCH_2CHOH^+). As a result, smaller alkanals with higher hydride ion affinities are more effective in abstracting hydride ions and in transfer hydrogenation ($C_4 > C_5 > C_6$). Propanal is an exception, as it is less effective in transfer hydrogenation than butanal. The deviation of propanal from the reactivity trend is apparently caused by its smaller transition state for hydride transfer, which is solvated to a lesser extent in FAU cages. The transfer hydrogenation occurs much more effectively on partially confined H^+ sites in FAU structures than in smaller pore MFI or unconfined $H_4SiW_{12}O_{40}$ polyoxometalate clusters, an indication that FAU solvates and stabilizes the bulky transition state of hydride transfer via van der Waals interactions. These effects of local site structures and the thermochemical properties of reactant determine the reactivity of alkanal transfer hydrogenation and thus selectivity ratio of alkenes, dienes, aromatics, and larger oxygenates during deoxygenation catalysis.

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1. Introduction

Brønsted acid sites (H^+) immobilized on solid matrixes catalyze the deoxygenation of light alkanals (RCH_2CHO , $R = CH_3$, C_2H_5 , or C_3H_7) in steps that involve inter-molecular or intra-molecular C=C bond formation, isomerization, dehydration, ring closure, and transalkylation reactions and form alkenes, dienes, alkenals, and aromatics at moderate temperatures (473–673 K) and ambient pressure, as established on H-MFI [1–4], H-Y [5], and $H_4SiW_{12}O_{40}$ polyoxometalate clusters [6]. Contained within these concurrent catalytic steps is the direct alkanal deoxygenation, which converts an alkanal reactant to the corresponding alkene ($RCH_2CHO + 2H \rightarrow RCHCH_2 + H_2O$) [1]. This reaction, in the absence of external hydrogen sources, must involve inter-molecular shuffling of hydrogen from reaction products to alkanal reactants, as required by the reaction stoichiometry. Despite the obvious involvement of reaction products as the hydrogen donors in these ubiquitous transfer

hydrogenation events, their mechanism and site requirements have not been clearly established.

Brønsted acid catalyzed hydride transfer has been studied extensively with density functional theory (DFT) calculations for the transfer from alkanes to alkenes on $H_3Si-OH-AlH_2-O-SiH_3$ clusters [7–9], from alkanes (e.g., propane and *t*-butane) to alkoxides (e.g., propyl and *t*-butyl alkoxides) in mordenite zeolite [10], and from alkanes (e.g., methane and ethane) to their corresponding carbenium ions (e.g., methyl and ethyl carbenium ions) in the gas phase [11]. It has also been probed experimentally between isobutane and cyclohexene on beta and ZSM-5 zeolites and on sulfated zirconia [12], during alkane crackings in zeolites (e.g., SAPO-41, ZSM-5, and Y) [13], and during dimethyl ether homologation on $H_4SiW_{12}O_{40}$ cluster, FAU zeolite, and mesoporous $SiO_2-Al_2O_3$ catalysts [14]. Hydride transfer on Brønsted acid occurs when a hydride ion donor (H-donor) donates a hydride ion to the hydride ion acceptor (H-acceptor) via the formation of a carbonium ion transition state sharing the hydride ion. An example of the H-donor is an alkane and of H-acceptor is either an adsorbed carbenium ion at the H^+ site [7,8,11,15] or an alkoxide [9,10,15] at the ground state [16–18]. The transition state decomposes when the H-acceptor

* Corresponding author. Fax: +1 (416) 978 8605.

E-mail address: cathy.chin@utoronto.ca (Y.-H. Chin).

desorbs while the H-donor becomes a carbenium ion and then donates its proton back to the catalyst surfaces, thus regenerating the H^+ site and completing the catalytic cycle [7,8]. Local confinement of the H^+ site appears to influence the hydride transfer reactivity [13,14]: hydride transfer from $n-C_5H_{12}$ to $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ carbenium ions is most effective when occurring inside zeolites with cavity volumes of $\sim 0.2 \text{ nm}^3$ [e.g., CIT-1 (0.211 nm^3) and MCM-68 (0.182 nm^3)] than those with either larger [e.g., MCM-22 (0.467 nm^3) and Y (0.731 nm^3)] or smaller [e.g., SAPO-41 (0.081 nm^3) and ZSM-5 (0.131 nm^3)] cavity volumes [13]. The reaction apparently requires its bi-molecular transition state to be at comparable dimensions with those of the zeolite cavities. In fact, the sums of the volumes for $(C_2H_5^+-n-C_5H_{10})$, $(C_3H_7^+-n-C_5H_{10})$, and $(C_4H_9^+-n-C_5H_{10})$ fragments are estimated to be 0.182, 0.203, and 0.224 nm^3 , respectively, in similar magnitudes with the cavities in CIT-1 and MCM-68 zeolites [13].

Large-pore FAU and BEA zeolites exhibit higher selectivities toward triptane than mesoporous $SiO_2-Al_2O_3$ and medium-pore MFI zeolites during solid acid catalyzed dimethyl ether homologation [14], because confinement within the larger pores preferentially solvates the larger transition states for hydride transfer and methylation and terminates the chain growth at C_7 products (triptane). Despite these extensive studies on the hydride transfer between alkanes and alkenes, few studies have addressed the hydride transfer to protonated carbonyl species. A recent study on hydrogen transfer and sequential dehydration of naphthols on H-Y zeolites has reported an increase in hydrogen transfer rates in the presence of hydrocarbons (e.g., tetralin and 1,5-dimethyltetralin), as these hydrocarbons may act as the hydrogen donors [19]. It is hypothesized that a hydride ion is being transferred from the H-donor to the keto tautomer of naphthol and the hydride ion dissociation energy of the H-donor influences the rate [19]. Little mechanistic details are available for the transfer hydrogenation of n -alkanal, despite the clear kinetic evidence of their predominant occurrences during their deoxygenation on solid Brønsted acid catalysts.

Here, we report catalytic insights and kinetic requirements for the transfer hydrogenation events, which shuffle hydrogen from H-donors, identified to be aromatic species (e.g., alkyl tetralins) or precursors to aromatics (e.g. alkyl cyclohexadienes), to protonated alkanals at Brønsted acid sites (H^+) in MFI and FAU zeolites or on polyoxometalate ($H_4SiW_{12}O_{40}$) clusters. We show that transfer hydrogenation occurs in a direct, concerted step between substituted tetralins or alkyl cyclohexadienes and protonated alkanals. The hydride donors are products of inter-molecular $C=C$ bond formation, ring closure, and dehydrogenation reactions. The hydride transfer reactivity exhibits a clear correlation with the hydride ion affinity differences between the carbenium ions of the H-donor and the H-acceptor and is a strong function of the extent of local structural confinements around the H^+ sites.

2. Experimental methods

2.1. Catalyst preparation

H-MFI and H-FAU zeolite samples were prepared by treating their NH_4^+ form (Zeolyst, CBV2314, $425 \text{ m}^2 \text{ g}^{-1}$, Si/Al atomic ratio = 11.5, $Na_2O = 0.05 \text{ wt.}\%$) and H^+ form (Zeolyst, CBV720, $780 \text{ m}^2 \text{ g}^{-1}$, Si/Al atomic ratio = 15, $Na_2O = 0.03 \text{ wt.}\%$), respectively, in flowing dry air (Linde, zero grade, $0.6 \text{ cm}^3 \text{ g}_{cat}^{-1} \text{ s}^{-1}$), by heating to 873 K at 0.0167 K s^{-1} and then holding isothermally at 873 K for 4 h. $H_4SiW_{12}O_{40}/SiO_2$ catalysts ($0.075 \text{ mmol H}_4SiW_{12}O_{40} \text{ g}_{SiO_2}^{-1}$) were prepared by dispersing $H_4SiW_{12}O_{40}$ (Sigma Aldrich, reagent grade, CAS #12027-43-9) on chromatographic SiO_2 (GRACE, $330 \text{ m}^2 \text{ g}^{-1}$, $0-75 \mu\text{m}$, $1.2 \text{ cm}^3 \text{ g}^{-1}$ pore volume, treated in air at

673 K for 5 h) via incipient wetness impregnation with a solution of $H_4SiW_{12}O_{40}$ and ethanol (Sigma-Aldrich, $>99.5\%$, anhydrous). The impregnated $H_4SiW_{12}O_{40}/SiO_2$ samples were held in closed vials for 24 h and then treated in flowing dry air (Linde, zero grade, $0.1 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) at 323 K (0.0167 K s^{-1} heating rate) for 24 h. The H^+ site densities on these catalysts ($\text{mol H}^+ \text{ g}_{cat}^{-1}$) were measured by pyridine titration at 473 K , as described in our previous work [1].

2.2. Rate and selectivity assessments

Alkanal conversion rates and site-time-yields of alkenes, dienes, oxygenates, and aromatics were measured in a fixed bed microcatalytic quartz reactor (9.5 mm inner diameter), which was loaded with 100 mg H-MFI or H-FAU zeolites or 50 mg $H_4SiW_{12}O_{40}/SiO_2$ powders supported on a coarse quartz frit. Catalysts were treated *in-situ* under flowing He (Linde, Grade 5.0, $8.3-16.7 \text{ cm}^3 \text{ g}_{cat}^{-1} \text{ s}^{-1}$) at 0.0167 K s^{-1} to the reaction temperature (573 K) prior to rate measurements. Alkanal or butanol reactant [butanal (Sigma Aldrich, puriss grade, $\geq 99\%$, CAS# 123-72-8), propanal (Sigma Aldrich, 97%, CAS# 123-38-6), pentanal (Sigma Aldrich, 97%, CAS# 110-62-3), hexanal (Sigma Aldrich, 98%, CAS# 66-25-1), or butanol (Sigma Aldrich, 99%, CAS# 71-36-3)] was introduced via a gas tight syringe (either 5 cm^3 Hamilton Model 1005 or 1 cm^3 SGE Model 008025), which was mounted on a syringe infusion pump (KD Scientific, LEGATO 100), into a vaporization zone heated to the boiling points of the respective reactants at atmospheric pressure, within which liquid alkanals were evaporated and mixed with He (Linde, Grade 5.0, $8.3-16.7 \text{ cm}^3 \text{ g}_{cat}^{-1} \text{ s}^{-1}$) or H_2 (Linde, Grade 5.0, $8.3 \text{ cm}^3 \text{ g}_{cat}^{-1} \text{ s}^{-1}$) purge stream. The mixture was fed to the reactor via heated transfer lines held isothermally at 473 K . Tetralin (Sigma Aldrich, 99%, CAS# 119-64-2), tetralin-adamantane mixture with a molar ratio of 20:1 (adamantane, Sigma Aldrich, 99%, CAS# 281-23-2), or cyclohexadiene (Sigma Aldrich, 97%, CAS# 592-57-4) was introduced into a second vaporization zone, which was located downstream of the zone for alkanal or alkanol vaporization described above, through a gas tight syringe (0.25 cm^3 SGE Model 006230) mounted on a syringe infusion pump (KD Scientific, LEGATO 100). This vaporization zone was maintained at 458 K for tetralin or tetralin-adamantane mixture infusion and 353 K for cyclohexadiene infusion. Chemical species in the reactor effluent stream were quantified with an online gas chromatograph (Agilent, Model 7890A) and mass spectrometer (Agilent, Model 5975C) by chromatographic separation with HP-5 (Agilent, 19091J-413, 30 m, 0.32 mm ID) or HP-5MS (Agilent, 190091S-433, 30 m, 0.25 mm ID) capillary columns. The HP-5 column was connected to thermal conductivity (TCD) and flame ionization (FID) detectors installed in series and the HP-5MS column to the mass spectrometer (MS). For each data point, the carbon balance, defined by the difference between the molar flow rates of all carbon species contained in the feed and the reactor effluent stream, was less than 10%.

3. Results and discussion

3.1. Alkanal deoxygenation pathways and the kinetic couplings of intra-molecular $C=C$ bond formation in alkanals and dehydrogenation of aromatic products at Brønsted acid sites

Catalytic pathways for alkanal (propanal [1,2] and butanal [6]) deoxygenation on solid Brønsted acid sites (H-MFI [1,2] and $H_4SiW_{12}O_{40}$ [6]) shown in Scheme 1 have been previously established based on selectivity changes with residence time and confirmed from reactions with the intermediates [2,6]. Butanal (C_4H_8O) deoxygenation occurs on Brønsted acid sites (H^+) via a

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