



Mechanistic insights on C–O and C–C bond activation and hydrogen insertion during acetic acid hydrogenation catalyzed by ruthenium clusters in aqueous medium



Junnan Shangguan^a, Mariefel V. Olarte^b, Ya-Huei (Cathy) Chin^{a,*}

^a Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Canada

^b Institute for Integrated Catalysis, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, USA

ARTICLE INFO

Article history:

Received 11 January 2016

Revised 29 April 2016

Accepted 30 April 2016

Available online 7 June 2016

Keywords:

Carboxylic acid
Hydrogenation
Ruthenium
Proton transfer
Aqueous phase catalysis
C–O bond activation
Hydrogen insertion
Reduction mechanism
Water solvation

ABSTRACT

Catalytic pathways for acetic acid (CH₃COOH) and hydrogen (H₂) reactions on dispersed Ru clusters in the aqueous medium and the associated kinetic requirements for C–O and C–C bond cleavages and hydrogen insertions are established from rate and isotopic assessments. CH₃COOH reacts with H₂ in steps that either retain its carbon backbone and lead to ethanol, ethyl acetate, and ethane (47–95%, 1–23%, and 2–17% carbon selectivities, respectively) or break its C–C bond and form methane (1–43% carbon selectivities) at moderate temperatures (413–523 K) and H₂ pressures (10–60 bar, 298 K). Initial CH₃COOH activation is the kinetically-relevant step, during which CH₃C(O)–OH bond cleaves on a metal site pair at Ru cluster surfaces nearly saturated with adsorbed hydroxyl (OH*) and acetate (CH₃COO*) intermediates, forming an adsorbed acetyl (CH₃CO*) and hydroxyl (OH*) species. Acetic acid turnover rates increase proportionally with both H₂ (10–60 bar) and CH₃COOH concentrations at low CH₃COOH concentrations (<0.83 M), but decrease from first to zero order as the CH₃COOH concentration and the CH₃COO* coverages increase and the vacant Ru sites concomitantly decrease. Beyond the initial CH₃C(O)–OH bond activation, sequential H-insertions on the surface acetyl species (CH₃CO*) lead to C₂ products and their derivative (ethanol, ethane, and ethyl acetate) while the competitive C–C bond cleavage of CH₃CO* causes the eventual methane formation. The instantaneous carbon selectivities toward C₂ species (ethanol, ethane, and ethyl acetate) increase linearly with the concentration of proton-type H^{δ+} (derived from carboxylic acid dissociation) and chemisorbed H*. The selectivities toward C₂ products decrease with increasing temperature, because of higher observed barriers for C–C bond cleavage than H-insertion. This study offers an interpretation of mechanism and energetics and provides kinetic evidence of carboxylic acid assisted proton-type hydrogen (H^{δ+}) shuffling during H-insertion steps in the aqueous phase, unlike those in the vapor phase, during the hydrogenation of acetic acid on Ru clusters.

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1. Introduction

Environmental and economic impacts have driven the bio-economy, which utilizes lignocellulosic biomass as a precursor instead of the conventional fossil based feedstock for fuel and chemical synthesis. Fast pyrolysis is a thermal chemical conversion route that transforms biomass to bio-oil, useful as a sustainable liquid energy carrier [1,2]. The bio-oil contains oxygenates with diverse functional groups (i.e., phenolic, carboxylic, furanic, carbonyl, alcohol functions), along with a large fraction of water [1,3]. Its high oxygen content lowers the heating value and thermal stability against polymerization and decomposition, thus making it

unsuitable to be used directly as a liquid fuel. Hydrotreating of bio-oil at high temperatures (673–778 K) and H₂ pressures (80–135 bar) removes the various functional groups, thus increasing the effective hydrogen-to-carbon ratios and heating values [4]. Hydrodeoxygenation of bio-oil at moderate temperatures (<673 K) and hydrogen pressures (<100 bar) remains as an attractive route, because such conditions minimize the cracking reactions of small oxygenates (e.g., acetic acid). Lower temperatures also prevent undesirable polymerization, which causes carbon losses from the liquid stream, catalyst deactivation, and undesirable operational shutdowns [5].

Catalytic hydrogenation of phenolic compounds [6–9], furanic compounds [10–12], and carboxylic acids [13–18] in aqueous media has remained as the subject of active research, as it is a critical step in bio-oil refining. Hydrogenation of carboxylic acids,

* Corresponding author.

E-mail address: cathy.chin@utoronto.ca (Ya-Huei (Cathy) Chin).

which transforms the acids to alcohols, is a crucial step to reduce the acid functionality and thus improve the stability of bio-oils. The rates of carboxylic acid hydrogenation [15,18] are at least an order of magnitude lower than those of carbonyl [19,20], phenolic [6,7,21], and furanic [10–12,20] compounds in the aqueous phase (e.g., turnover rates of $2.1 \times 10^1 \text{ h}^{-1}$ for acetic acid on Ru/C [18] vs. $2.1 \times 10^3 \text{ h}^{-1}$ for acetaldehyde on Ru/Al₂O₃ [20] at 373 K, turnover rates of 1.0 h^{-1} for acetic acid [18] vs. $4.2 \times 10^3 \text{ h}^{-1}$ for phenol [21] on Pd/C at 473 K). Hydrogenation of acetic acid, the simplest carboxylic acid, over supported transition metals or metal oxides produces acetaldehyde and ethanol (Pt/TiO₂ [22], Fe/SiO₂ [23], Fe/C [23], Cr₂O₃ [24], and Fe₂O₃ [23–25]), methane and carbon oxides (CO and CO₂) (Pt/SiO₂ [26,27]), and acetone (Fe/C [23], ZrO₂ [24], CeO₂ [24], ZnO [24], and MnO [24]) in the vapor phase. This reaction, when carrying out in the aqueous phase, requires catalysts that are stable at high temperatures and in acidic solution. Transition metals (Raney Ni [18], Raney Cu [18], Ru/C [16,18], Ru/ZrO₂ [15], Ru/Al₂O₃ [15], Pd/C [18], Pt/C [13,18], and Pt/TiO₂ [13]) are active catalysts for hydrogenation reactions in the aqueous phase, especially dispersed Ru clusters, which selectively convert acetic acid to ethanol with carbon selectivities as high as 70% (at 373–573 K, 10–50 bar H₂, with methane, ethane, and ethyl acetate as the side products) [13–18]. The reaction pathways and their detailed mechanism leading to the formation of ethanol and the various side products have not yet been unequivocally established. Density Functional Theory (DFT) was used to elucidate the activation and hydrogenation of acetic acid on Group VIII metal surfaces {Pt(111) [18,28], Pd(111) [18,29–31], Ru(0001) [16,18,32]}, but these theoretical calculations were developed for vapor phase reactions and surfaces free of reactive intermediates, and thus cannot be directly applied to describe the reaction energetics for acetic acid hydrogenation in the aqueous medium. Metal surfaces during the aqueous phase reactions are predominantly covered with hydroxyl species and activation enthalpies and entropies are influenced largely by water solvation and hydrogen bonds. Specifically, a rigorous, quantitative explanation on the relative site-time-yields for ethanol and methane, the extents of several side reactions, the coverages and catalytic roles of surface intermediates, the specific role of H₂O molecules (solvent), and their temperature dependence have remained elusive.

Here, we report the catalytic pathways and the associated kinetics during acetic acid hydrogenation (CH₃COOH–H₂) in the aqueous phase that lead to the formation of ethanol, other C₂ side products such as ethyl acetate and ethane, and methane at moderate temperatures (413–523 K) and hydrogen pressures (10–60 bar H₂, measured at 298 K). We propose a closed sequence of elementary steps, which encompasses the initial CH₃C(O)–OH cleavage, followed by sequential H-insertion reactions with either H adatom (H*) or proton (H⁺), the latter is afforded by the additional catalytic role of CH₃COOH as a proton-shuffling catalyst, or by the competing C–C bond cleavage step on Ru cluster surfaces covered predominantly with hydroxyl species. We interpret the observed activation barrier required for CH₃COOH activation into energetic contributions from the kinetically-relevant step and heats of adsorption of the reactive intermediates, and gas phase bond dissociation energies (BDE), considering the H₂O solvation effects and the predominant site occupation by OH* species. We find that increasing the reaction temperature largely promotes the undesirable C–C bond cleavage step that leads to methane, because of its higher observed barrier than those of H-insertions. This work offers mechanistic insights for the hydrogenation of carboxylic acid (CH₃COOH) and demonstrates a specific route for carboxylic acid facilitated proton (H⁺) addition onto the surface acetyl species on dispersed Ru clusters in the aqueous medium.

2. Experimental methods

2.1. Synthesis and characterizations of Ru clusters supported on activated carbon powders

Activated carbon powders [Norit, Activated Carbon, SX ULTRA CAT 8020-1, 1200 m² g⁻¹, 90% of the particles (*D*₉₀) are <100 μm, pore volume of 1.4 cm³ g⁻¹] were loaded into a quartz boat, placed in a muffler furnace, and then treated under flowing He (Linde certified standard, 99.999%, 0.60 cm³ g⁻¹ s⁻¹) by increasing the temperature at 0.03 K s⁻¹ to 573 K, holding for 7 h, and then cooled to 298 K before Ru incorporation (4 wt.%) by incipient wetness impregnation method. The incipient wetness impregnation was carried out via two consecutive impregnation steps. Within each step, an aqueous Ru precursor, prepared from mixing Ru(NO)(NO₃)₃ (Sigma Aldrich, 1.2 wt.% Ru, CAS Number: 34513-98-9) with doubly-deionized water (>18 MΩ cm), was added dropwise to the carbon powder. After each impregnation step, the sample was placed in the ambient environment for 12 h before further heating from ambient environment to 348 K and keeping at 348 K for another 12 h. The fully-impregnated sample was treated under flowing 5% H₂/He (Linde certified standard, 0.27 cm³ g⁻¹ s⁻¹) by heating at 0.16 K s⁻¹ to 723 K for 5 h. The sample was then cooled to ambient temperature (~0.08 K s⁻¹) under flowing of 5% H₂/He (Linde certified standard, 0.27 cm³ g⁻¹ s⁻¹) while purging with He (Linde certified standard, 99.999%, 0.10 cm³ g⁻¹ s⁻¹) for 1 h, before exposure to flowing 5.5% O₂ (Linde certified standard, 0.15 cm³ g⁻¹ s⁻¹) at 298 K for 1 h. The sample was then exposed to ambient air.

The mean Ru cluster diameter was determined from the amount of irreversibly adsorbed H₂, measured with a volumetric adsorption-desorption apparatus over 0–13 kPa H₂ at an incremental pressure of ~495 Pa at 313 K. The catalyst was treated *in-situ* in flowing H₂ (Linde, 99.99%, 0.8 cm³ g⁻¹ s⁻¹), by heating from ambient temperature to 723 K at 0.03 K s⁻¹ and holding isothermally at 723 K for 1 h before exposing to dynamic vacuum (<5 × 10⁻² Pa) at 723 K for at least 12 h and then cooling to 313 K for the H₂ uptake measurements. Two sets of H₂ uptakes were measured, and between them, the catalyst was evacuated under dynamic vacuum (1 × 10⁻⁶ Pa to 5 × 10⁻² Pa) for 5 min at 313 K. The amount of irreversibly adsorbed H₂ was determined by the difference between the H₂ uptakes obtained from extrapolating the two isotherms to zero pressures. Mean cluster diameter (*d*_{avg}) was obtained by assuming an atomic ratio for chemisorbed H-to-surface Ru of unity and calculated based on the following equation [33]:

$$d_{\text{avg}} = \frac{6v_m}{Da_m} \quad (1)$$

where *v*_m (13.65 × 10⁻³ nm³ [28,33]) is the average volume occupied by a single Ru-atom in the bulk phase, *a*_m (9.9 × 10⁻² nm² [28]) is the average surface area occupied by an exposed Ru surface atom, and *D* is the dispersion (atomic ratio of surface to bulk Ru). The number 6 in the equation comes from the hemispherical cluster assumption. The dispersion value was 7.0% and the mean cluster diameter was 13 nm.

2.2. Rate and selectivity assessments with an isothermal, ideal batch stirred tank reactor

Rates and selectivities for CH₃COOH–H₂ reactions in the aqueous phase were measured with an isothermal batch stirred tank reactor equipped with a mechanical stirrer (300 cm³, Parr Instrument 4560 Mini Bench Top Reactors, Hastelloy). Acetic acid aqueous solution [0.00–3.33 M (mol dm⁻³), 100 cm³ mixture of acetic

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