



Microkinetic analysis of C₃–C₅ ketone hydrogenation over supported Ru catalysts



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ABSTRACT

Rates of C₃–C₅ ketone hydrogenation are measured in the vapor phase over Ru/SiO₂. Reaction kinetics are considered through a range of ketone partial pressures (0.3–30 Torr), hydrogen partial pressures (90–900 Torr), and reaction temperatures (322–456 K). Ketone hydrogenation is observed to be facile, with site time yields ranging from 0.14 s⁻¹ for 2-pentanone to 0.37 s⁻¹ for acetone at 322 K and 1.2 bar H₂. At low temperatures, apparent reaction orders and kinetic barriers are similar for all ketones. During acetone hydrogenation at higher temperatures, (422 K), the ketone order increases from 0 to 0.4, while the hydrogen order increases from 0.5 to 0.9. Furthermore, the apparent barrier decreases from ≈50 kJ mol⁻¹ at 322 K to ≈18 kJ mol⁻¹. Apparent trends in hydrogenation rates are interpreted at an elementary level using a microkinetic analysis that is based on a Horiuti–Polanyi mechanism involving two distinct surface sites.

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1. Introduction

In the interest of producing sustainable industrial commodities, catalytic technologies for biomass refining are receiving increased attention. Since biomass is heavily oxygenated relative to most petroleum-derived products, such approaches are often based on reductive chemistries. A commonly encountered example is the metal-catalyzed hydrogenation of carbonyl groups (C=O) to their corresponding hydroxyl groups (CH–OH), which facilitates the targeted production of alcohols. Biorefining applications that require selective carbonyl reduction include the hydrogenation of furfural to produce furfuryl alcohol [1], the hydrogenation of 5-hydroxymethylfurfural (HMF) to produce 2,5-di-hydroxy-methyl-tetrahydrofuran (DHMF) [2], and the hydrogenation of glucose to sorbitol [3,4]. Finally, carbonyl reduction is central to the production of γ -valerolactone (GVL) from levulinic acid (LA), which facilitates a number of practical strategies that are able to connect lignocellulosic sugars with commodity markets [5–10]. Despite the recent popularity of LA hydrogenation, the community is lacking a quantitative, elementary description of reaction kinetics and catalyst performance in this system, which limits our ability to

rationally design active and stable materials tailored for the reduction of LA.

Because of its reactivity and low vapor pressure, LA hydrogenation is generally performed in condensed media, where Ru-based catalysts [11] consistently deliver good GVL selectivity at high LA conversions [7,9,10,12,13]. Unfortunately, kinetic analysis of this system is challenging. Liquid-phase reactions present a number of practical and fundamental difficulties, each of which obscure the elementary phenomena that are, as kineticists, our primary interests. For example, the presence of a condensed phase may induce various modes of deactivation [3,5,6,8,14,15], cause active site restructuring [3,6,8,14], severely constrain rates of mass diffusion [16,17], and force one to consider the implications of thermodynamic non-idealities [18,19]. Accordingly, elementary kinetic analysis can be challenging for heterogeneously catalyzed reactions occurring in the liquid phase.

Relative to condensed media, the confounding effects of deactivation, restructuring, mass transfer, and solvation can be substantially mitigated in the vapor-phase; therefore, vapor-phase reactions are generally a more appropriate choice for framing a fundamental kinetic analysis of a given system. Unfortunately, generating sufficient partial pressures of levulinic acid over a wide temperature range (298–456 K) is nontrivial, if not impossible, which makes detailed, vapor-phase kinetic analysis of levulinic acid hydrogenation intractable. Recently, we demonstrated that the rates of levulinic acid hydrogenation and 2-pentanone

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hydrogenation are identical in water [6]. This suggests that LA hydrogenation can be viewed as a specific example of a generic ketone hydrogenation, which is a generally feasible system for vapor-phase analysis. Accordingly, a reasonable first step in understanding the kinetics of LA hydrogenation is to define expectations for ketone hydrogenation in the vapor phase. Once established, one may then view the complexities of solution-phase ketone hydrogenations as perturbations to this idealized framework. Our effort here is therefore focused on establishing and reconciling a universal, microkinetic description of vapor phase C₃–C₅ ketone hydrogenation on supported Ru catalysts. Ultimately, the hope is that this will both aid in the rational design of supported metal hydrogenation catalysts and provide a foundation for subsequent analysis of solvent effects in metal-catalyzed hydrogenations.

2. Experimental

2.1. Materials and methods

Acetone (99 + %, Acros Organics), 2-butanone (99 + %, Acros Organics), 2-pentanone (99%, Acros Organics), isopropyl alcohol (reagent grade, Acros Organics), 2-butanol (99%, Alfa Aesar), and 2-pentanol (98%, Acros Organics) were used as reactor feeds and/or for instrument calibration. Catalysts were synthesized using ruthenium (III) chloride hexahydrate (35–40% Ru, Acros Organics) and amorphous SiO₂ (481 m²/g, Sigma Aldrich). H₂ (99.999%, Airgas), He (99.999%, Airgas), N₂ (99.999%, Airgas) and CO (99.99% Praxair) were employed in kinetic studies, catalyst pretreatment, and catalyst characterization. 5% H₂ and 5% D₂ blends in 1% Ar with a He balance (Airgas) were used in isotope switching experiments. Each reagent was used as supplied by the manufacturer. Water used in preparation of catalysts was purified in house by reverse osmosis, UV oxidation, and ion exchange to achieve a resistivity equal to at least 18.2 MΩ cm⁻¹.

2.2. Catalyst preparation

Ru/SiO₂ catalysts were prepared by incipient wetness impregnation of amorphous SiO₂ with aqueous ruthenium (III) chloride hexahydrate. SiO₂ was selected because it is devoid of strong acid/base functionality, and reference experiments confirmed it to be inert to both feed molecules (2-ketones) and products (2-alcohols) under reaction conditions. An incipient volume of 1.6 ml of solution per gram of support was used. Impregnated catalysts were dried in air at 393 K overnight and subsequently reduced in flowing H₂ (100 ml min⁻¹, 673 K, 3 K min⁻¹). Prior to removal from reduction vessels, samples were passivated at 298 K in a stream of 1% O₂ in He.

2.3. Catalyst characterization

Catalyst surface area and porosity were probed by N₂ physisorption at 77 K (Micromeritics ASAP 2020). Before N₂ dosing, samples were outgassed under vacuum (6 h, 523 K). Total surface areas and pore size distributions were obtained through BET and BJH analyses of the N₂ adsorption/desorption isotherm. Pore volumes were estimated from the total N₂ uptake at a relative pressure of 0.995.

Ru surface site densities were quantified by CO adsorption at 308 K (Micromeritics ASAP 2020). Prior to dosing, samples were reduced in flowing H₂ (3 h, 673 K, 3 K min⁻¹), evacuated at 673 K for 1 h to remove chemisorbed hydrogen, and cooled to 308 K under vacuum. The analysis was then performed at 308 K by collecting an adsorption isotherm, evacuating the sample for 1 h to remove physisorbed CO, and collecting a second isotherm.

Irreversible CO uptake was determined from the difference in CO adsorption between the first and second isotherms. Here, irreversible CO uptake was taken as equivalent to the Ru surface site density, which assumes a CO adsorption stoichiometry of 1.

2.4. Catalytic activity testing

Hydrogenations of acetone, 2-butanone, and 2-pentanone were carried out in a downflow, packed bed reactor. Catalyst particle sizes were restricted to the 45–90 μm range to minimize length scales for intraparticle diffusion. Carbonyl hydrogenation is exothermic (≈–55 kJ mol⁻¹). As a precaution against localized heating, active catalysts (Ru/SiO₂) were diluted 10–20:1 (diluent: catalyst) in amorphous SiO₂ (45–90 μm). This admixture was loaded into a 6.35 mm OD 316 stainless steel tube, and the bed was held in place by quartz wool plugs. The void volume below the catalyst bed was packed with 850–2000 μm quartz chips. Prior to kinetic analysis, the catalyst bed was reduced in situ under H₂ (100 sccm) at 673 K for 4 h with a ramp rate of 5 K min⁻¹. The bed was then cooled to the desired reaction temperature under a continuous H₂ purge. Reactor temperature was monitored and controlled at the outer wall of the packed bed using a Type K thermocouple and a PID temperature controller (LOVE 16A 3010). Kinetic data are reported at the bed temperature, which was measured by an auxiliary, in-line Type K thermocouple positioned in the void space just above the catalyst bed.

During kinetic experiments, gaseous reactor feeds (He and H₂) were regulated using mass flow controllers (Brooks 5850S). Liquid ketones were introduced using a syringe pump (Cole-Parmer series 100) and fed through a 130 μm PEEK capillary into a heated vaporization chamber where they were contacted with pre-heated gas feeds. Ketone partial pressures were maintained below 15% of their saturation pressure to ensure complete vaporization of the liquid feed. The combined feed was then passed through a temperature-controlled static mixer, where it was pre-heated to reaction temperature. During reactor startup, the feed stream was diverted through a bypass and monitored using online GC analysis. Upon reaching steady state, the feed stream was introduced into the reactor, and the point of valve switching was taken as zero time on stream. Ketone co-feeding experiments were performed by adding a second vaporization unit.

Quantitative product analysis was achieved using an on-line Agilent 7890 GC equipped with a 6-port gas sampling valve, an HP-INNOWAX column, and an FID detector. This configuration permitted resolution and quantification of all ketones and alcohols considered in this study. The identities of products and reactants were confirmed using an Agilent 7890 GC-MS equipped with an Agilent 5975C MS detector and an HP-INNOWAX column. All kinetic data reported here were obtained with complete carbon balance closure. After an initial transient period of roughly two minutes on stream, carbon balances closed to at least 95%. After achieving carbon balance closure, we began collecting the kinetic data summarized in the remainder of this manuscript. Residence times in each experiment were adjusted to maintain ketone conversions below 11%. The anticipated equilibrium ketone conversion exceeds 96% under all reaction conditions reported here. Accordingly, all production rate data were obtained at or below roughly 12% of the equilibrium limit, which allows the conclusion that kinetic data reflect differential operation and that measured production rates represent the forward rate of ketone hydrogenation under all experimental conditions.

To allow for meaningful comparisons among catalysts having varied metal loadings, hydrogenation rates are reported on a per-site basis as the total site time yield (STY) of hydrogenation products:

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