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.

Keywords

Ketone hydrogenation kinetics; Ruthenium; Microkinetic modelling; vapor phase hydrogenation; Horiuti-Polanyi

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] which 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 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 SiO_2 (481 m^2/g , Sigma Aldrich). H_2 (99.999%, Airgas), He (99.999%, Airgas), N_2 (99.999%, Airgas) and CO (99.99% Praxair) were employed in kinetic studies, catalyst pretreatment, and catalyst characterization. 5% H_2 and 5% D_2 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 $\text{M}\Omega \text{ cm}^{-1}$.

2.2 Catalyst preparation

Ru/ SiO_2 catalysts were prepared by incipient wetness impregnation of amorphous SiO_2 with aqueous ruthenium (III) chloride hexahydrate. SiO_2 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 H_2 (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% O_2 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 1h 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 H_2 (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 H_2 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 K-type thermocouple positioned in the void space just above the catalyst bed.

During kinetic experiments, gaseous reactor feeds (He and H_2) were regulated using mass flow controllers (Brooks 5850S). Liquid ketones were introduced using a syringe pump (Cole-Parmer series 100) and fed through a $130 \text{ }\mu\text{m}$ 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:

$$STY_i = \frac{\sum_j F_j}{S_{R_i}} \quad (1)$$

In Eq. (1), F_j is the effluent molar flowrate of an individual hydrogenation product—a C₃ to C₅ alcohol—and S_R is the total molar quantity of Ru surface sites in a given catalyst bed as estimated by CO chemisorption. Baseline activity was measured over amorphous SiO₂; no extent of ketone hydrogenation or alcohol dehydrogenation were observed in the absence of Ru. Across all catalysts, reaction conditions, and extents of deactivation, 2-ketone hydrogenation was 100% selective to the secondary alcohol. We did not observe secondary hydrogenolysis of the alcohol to form its corresponding alkane under any reaction conditions.

During vapor-phase ketone hydrogenation, the activity of Ru/SiO₂ decays rapidly with time-on-stream (see online supporting information). Prior to further interpretation, it is worth considering

whether this transient behavior is associated with the anticipated dynamics of a catalyst surface approaching steady state or with catalyst deactivation. According to Boudart [20], the time required for a catalytic reaction to reach steady state can be estimated by the inverse of the turnover frequency for that reaction. Under steady state conditions at 303K (the lowest temperature and thus lowest rate in this study), we measured site-time-yields of roughly 0.05 s^{-1} . Based on this conservative, “steady state” rate, we estimate that transient behavior should die off after 30 to 60 seconds at the lowest temperature of the study. This is consistent with our observation that we are able to achieve full mass and carbon balance closure within 2 minutes time on stream under all reaction conditions. Decay profiles persist over a period greater than 100 minutes on stream; accordingly, we attribute the observed decline in reaction rate as a function of time on stream to catalyst deactivation. Since ex-situ characterization methods were used to titrate surface sites, meaningful STYs and structure-activity relations are generated only by estimating the rate of reaction at zero time-on-stream, which can be correlated with CO uptake on pristine catalysts. Accordingly, *all* absolute hydrogenation rates reported in this manuscript were corrected to zero time on stream using the approach described in the online supporting information.

3. Results

3.1 Catalyst synthesis & characterization

Ru clusters were supported on amorphous SiO_2 at a range of loadings. Physicochemical properties of these catalysts are summarized in Table 1. Although CO uptakes change substantially, Ru dispersions are relatively uniform, suggesting similar cluster sizes and structures despite variation in metal surface area.

Table 1. Physical properties and irreversible CO uptake measurements of various supported Ru/SiO₂ catalysts.

Ru wt% ^a	SA (m ² g ⁻¹)	Pore Diameter (Å) ^b	Irreversible CO uptake (μmol g ⁻¹)	CO _{irr} /Ru	d _p (nm) ^c
0	481	56.5	-	-	-
0.3	471	49.9	11	0.36	3.9
0.6	514	48.6	15	0.25	5.7
0.84	494	50.1	35	0.42	3.4
1.5	520	49.9	62	0.41	3.5

a - Based upon concentrations of impregnating solutions, incipient volume, and support mass.

b - Average pore diameter determined by BJH analysis of N₂ adsorption/desorption data.

c - Calculated assuming Ru has a shape factor of 6, an atomic cross-sectional area of 6.14 Å² and a density of 12.30 g cm⁻³.

3.2 Assessing kinetic control

The extent of kinetic control was examined by applying the Koros-Nowak criteria to hydrogenation rates estimated at zero time on stream for acetone and 2-pentanone [21, 22], which represent the two systems most likely constrained by mass diffusion. Specifically, acetone exhibited the highest rate of hydrogenation per unit mass of catalyst, and 2-pentanone, the largest molecule considered, had the smallest diffusivity. Strictly speaking, this analysis should be applied only to catalysts having identical metal particle size such that one may avoid the potentially obscuring influences of structure sensitivity. Based on data in Table 1, we do not rigorously satisfy this criterion; however, we believe the test can still be applied. First, particle sizes estimated by CO chemisorption (Table 1) indicate that Ru clusters, with the exception of those in the 0.6 wt% sample, are effectively indistinguishable, suggesting a single outlier in terms of metal dispersion. Second, we have previously demonstrated that levulinic acid hydrogenation over Ru is structure-insensitive over 1.7 – 4.0 nm clusters [6], and literature generally concludes that carbonyl hydrogenations are a structure-insensitive class of reactions.[23] Thus, Ru surface sites in particles ranging from 3.0 – 6.0 nm should be kinetically

indistinguishable, allowing us to use the Koros-Nowak test in assessing kinetic control for the present system.

Results are summarized in Fig. 1, which plots initial (zero-time), mass-normalized hydrogenation rates for acetone and 2-pentanone against irreversible CO uptake on logarithmic axes at 322 and 341 K. The slope of the regression lines for acetone and 2-pentanone are near unity at both temperatures, indicating a system free of both mass and heat transfer limitations per Madon and Boudart [22]. Because rates of 2-butanone hydrogenation never exceed those of acetone hydrogenation and because 2-butanone diffusion should be at least as fast as that of 2-pentanone, we assume that 2-butanone hydrogenation rates are also kinetically controlled. Furthermore, because of the pronounced catalyst deactivation in this system, the initial rates illustrated in Fig. 1 represent the highest *measured* absolute hydrogenation rates per unit mass of catalyst under any experimental condition. *Reported* rates in this manuscript always reflect the initial rate of reaction prior to the onset of deactivation and, in many cases (e.g., at high temperatures), they exceed reaction rates where it would be feasible to maintain kinetic control. However, *measured* rates were collected over substantially deactivated catalyst beds, where volumetric reaction rates were always lower than those reported in Fig. 1, and subsequently *corrected* to zero time on stream. Thus, initial rates reported here represent hypothetical, kinetically-controlled rates at zero time on stream.

Figure 1: Functional relationship between mass-normalized ketone hydrogenation rates and Ru surface site densities as determined by CO chemisorption. Hydrogenation rates were measured at 4.8 Torr ketone and 910 Torr H_2 , open and closed symbols indicate rates at 322 K and 341 K respectively. For (a) acetone hydrogenation, the slope of the regression lines indicated in the figure are 1.04 ± 0.11 (322K) and 1.1 ± 0.9 (341K). For (b) 2-pentanone hydrogenation, the slope of the regression lines indicated in the figure are 0.96 ± 0.30 (322K) and 1.1 (341K). This is consistent with criteria given by Koros and Nowak for demonstration of kinetically controlled hydrogenation rates at the given temperatures. Confidence intervals were calculated at a 95% confidence level.

Results of the Koros-Nowak analysis (Fig. 1) indicate that each Ru/SiO₂ sample in this series displays an identical site time yield during ketone hydrogenation. Accordingly, all kinetic data presented hereafter represent the average site time yield measured over several Ru/SiO₂ samples having varied metal loading. Average site time yields obtained at 322K are summarized for acetone (Entry 1), 2-butanone (Entry 2), and 2-pentanone (Entry 3) in Table 2. Data in Table 2 show that ketone hydrogenation rates decrease with the length of the carbon chain such that the rate of acetone hydrogenation > 2-butanone hydrogenation > 2-pentanone hydrogenation.

Table 2: Initial STY of hydrogenation of various ketones measured at 322 K, 4.8 Torr of ketone and 910 Torr of H_2 . Confidence intervals are calculated at 95%.

Ketone	Average initial STY ^a (s^{-1})
Acetone	0.37 ± 0.04
2-butanone	0.33 ± 0.02
2-pentanone	0.14 ± 0.04

a- Site time yields represent the average over multiple Ru/SiO₂ catalysts with varied metal loading.

3.3.1 Apparent Kinetics of ketone hydrogenation: low temperatures

Fig. 2 illustrates the dependence of hydrogenation rates on ketone partial pressure (Fig. 2a) and hydrogen partial pressure (Fig. 2b) for acetone, 2-butanone, and 2-pentanone at 322K. Over the partial pressure ranges considered, rates of hydrogenation for each ketone exhibit an apparent zero order dependence on the ketone and an apparent half-order dependence on H_2 .

Figure 2: Effect of (a) ketone and (b) hydrogen partial pressure on the site time yield of hydrogenation at 322 K for (○) 2-pentanone, (□) 2-butanone and (Δ) acetone. Ketone partial pressures varied from approximately 0.3 – 30 Torr. Hydrogen partial pressures varied from 90-910 Torr.

As illustrated in Fig. 3, the apparent barrier for hydrogenation is approximately 50 kJ mol⁻¹ for all C₃-C₅ ketones in the range of 303-359 K, which is consistent with previously reported apparent barriers for acetone hydrogenation over supported group VIII metals [23-25].

Figure 3: Arrhenius plot for ketone hydrogenation from 303 - 359 K at a ketone and hydrogen partial pressure of 4.8 and 910 Torr respectively for (○) 2-pentanone, (□) 2-butanone and (Δ) acetone.

This suggests that differences in rates observed between acetone, 2-butanone, and 2-pentanone arise from differences in adsorbate surface coverages and/or pre-exponential factors (activation entropies); however, further interpretation is difficult at this stage, and we defer in depth discussion to subsequent microkinetic analysis (Section 4.5). Apparent reaction orders and kinetic parameters for the individual ketones are summarized in Table 3.

Table 3. Summary of apparent activation barriers and reaction orders based for the various ketones studied over supported Ru/SiO₂ catalysts. Activation barriers were determined at 4.8 and 910 Torr of ketone and H₂ respectively. Reaction orders were determined at 322 K. Confidence intervals calculated at 95%.

Ketone	Average STY (s ⁻¹) ^a	A (Torr ^{-0.5} s ⁻¹) ^b	E _a (kJ mol ⁻¹)	Ketone reaction order	H ₂ reaction order
2-pentanone	0.14 ± 0.04	2.1 × 10 ⁷	49.5 ± 5.2	0.01 ± 0.18	0.52 ± 0.14
2-butanone	0.33 ± 0.02	9.5 × 10 ⁷	51.8 ± 5.0	-0.01 ± 0.01	0.57 ± 0.12
Acetone	0.37 ± 0.04	4.8 × 10 ⁷	50.1 ± 2.3	0.03 ± 0.22	0.48 ± 0.08

a- Reaction conditions of 322 K, 4.8 Torr ketone, 910 Torr H₂. Average across multiple catalysts and Ru loadings

b- Calculated assuming an apparent power law expression $r = Ae^{\frac{E_a}{RT}}P_{H_2}^{0.5}$

3.3.2 Apparent Kinetics of ketone hydrogenation: high temperatures

A goal of this study is to provide an elementary rationale for differences in observed macroscopic rates of hydrogenation for $C_3 - C_5$ ketones. To reveal adsorbate coverage effects that may underlie variations in site time yield, it is necessary to experimentally depart from the regime of (ketone) saturation kinetics described in the preceding section. To this end, an analogous set of high temperature kinetic data were collected for acetone hydrogenation. Specifically, rates of acetone hydrogenation were measured between 303 and 456 K at 4.8 Torr acetone and 910 Torr hydrogen. Reaction orders were probed by varying both ketone and hydrogen partial pressures at 442 K.

Figure 4: Arrhenius plot for acetone hydrogenation from 303 - 456 K at ketone and hydrogen partial pressures of 4.8 and 910 Torr.

Fig. 4 illustrates the trend in hydrogenation rates as a function of inverse temperature over this larger span. At lower temperatures, an apparent barrier of $\approx 50 \text{ kJ mol}^{-1}$ is again observed. This barrier (evidenced by linearity) extends to roughly 418 K ($1000/T = 2.4 \text{ K}^{-1}$), at which point the

apparent barrier begins to decrease, ultimately approaching zero as temperatures near 456 K ($1000/T = 2.2 \text{ K}^{-1}$). Although plausible, we do not believe this observed decrease is attributed to the onset of mass transfer limitations. Again, rates in this experiment were measured over a deactivated catalyst, and volume-normalized rates were always well below initial rates that have been proven to be kinetically controlled (see Section 3.2).

Figure 5: Effect of (a) ketone and (b) hydrogen partial pressure on the site time yield of acetone hydrogenation at 442 K. Ketone partial pressures varied from 0.5 – 4.8 Torr. Hydrogen partial pressures varied from 250-910 Torr.

Fig. 5 illustrates the response in hydrogenation rate to variations in ketone and hydrogen partial pressure at 442 K. Relative to trends at 322 K, the apparent reaction orders for acetone and hydrogen increase, respectively, to 0.40 ± 0.12 and 0.92 ± 0.09 . This observation is consistent with more sparsely covered Ru surfaces at higher temperatures, which may explain the decrease in apparent barrier at high temperatures: as the coverage of vacant sites increase, apparent barriers become increasingly influenced by exothermic heats of adsorption. Generally, this will manifest as a decrease in apparent barriers compared to those observed in regimes of saturation kinetics.

3.3.3 Apparent Kinetics of ketone hydrogenation: co-feeding conditions

To further probe the source of macroscopic differences in site-time yield between acetone, 2-butanone, and 2-pentanone, a series of experiments were performed wherein 2-pentanone hydrogenation rates were measured while co-feeding acetone and 2-butanone at 1:1 and 5:1 molar ratios. Perturbations to the hydrogenation rate from experiments with isolated ketone feeds provide insight into competitive adsorption and coverage effects. Since equilibrium coverages (for a fixed partial pressure) are determined by adsorption thermodynamics, this experiment will aid in resolving differences in adsorption energetics for each ketone during our subsequent microkinetic analysis (Section 4.5).

Table 4 summarizes rates of 2-pentanone hydrogenation at 322 K in the presence of acetone (Entries 1 and 2) and 2-butanone (Entries 3 and 4). Here, hydrogenation rates are normalized to those obtained for 2-pentanone in isolation (Section 3.3.1). In all cases, 2-pentanone hydrogenation rates decrease upon introducing a second ketone, which is consistent with competitive adsorption of ketones and/or their hydrogenated derivatives at surface metal sites. Interestingly, for equivalent partial pressures of the co-feed, 2-butanone leads to a larger reduction in 2-pentanone hydrogenation rates than acetone, implying a larger decrease in C_5 surface coverages with the 2-butanone co-feed. Tentatively, this may be attributed either to a more favorable adsorption free energy of 2-butanone or to steric factors associated with the longer carbon chain (C_4) relative to acetone (C_3), which could plausibly lead to increased site blocking for 2-pentanone adsorption.

Table 4. Summary of relative 2-pentanone hydrogenation rates at 322 K in the presence of different ketones over supported Ru/SiO₂ catalysts.

Ketone co-feed	P _{2-pentanone} (Torr)	P _{co-feed} (Torr)	$\frac{r_{2\text{-pentanone,co-feed}}}{r_{2\text{-pentanone}}}$
Acetone	4	4	0.81
Acetone	4	20	0.47
2-butanone	4	4	0.66
2-butanone	4	20	0.28

4. Discussion

4.1 Elementary surface steps

Because of the similarity in overall chemistry, apparent reaction orders, and apparent kinetic parameters at low temperatures, it is reasonable to assume that the hydrogenation of each C₃-C₅ ketone can be described by a common set of elementary steps. The kinetics of carbonyl hydrogenation are generally interpreted in the context of the Horiuti-Polanyi mechanism, which is predicated on step-wise addition of hydrogen adatoms to an unsaturated, surface-bound hydrocarbon [24, 26-28]; however, there remains some uncertainty regarding the site requirements for this process on a given metal surface. In separate studies, hydrogenation kinetics have been reconciled with schemes in which the rate controlling step involves a reaction between a hydrogen atom and a hydrocarbon fragment that are both bound at a *single* type of active site [24] and schemes in which the rate controlling step involves a reaction between a hydrogen atom and a hydrocarbon fragment that are bound at *distinct* types of active sites [23, 25]. Because neither model can be excluded a priori, we consider both prior to framing a more fundamental analysis.

4.2 Single site model

The conventional Horiuti-Polanyi scheme, applied to ketone hydrogenation, is presented as the series of elementary steps shown in Table 5. In this case, we consider that all adsorption and reaction steps involve a single type of active site, which is designated here as ‘*’.

Table 5. Proposed set of elementary steps to describe ketone hydrogenation over Ru surfaces.

Elementary step	Surface Reaction
1.	$K + * \xrightleftharpoons{K_1} K_*$
2.	$H_2 + 2* \xrightleftharpoons{K_2} 2H_*$
3.	$K_* + H_* \xrightleftharpoons{K_3} KH_* + *$
4.	$KH_* + H_* \xrightleftharpoons{K_4} A_* + *$
5.	$A_* \xrightleftharpoons{K_5} A + *$

In this sequence, the ketone (K) adsorbs molecularly at a metal site ($*$), while hydrogen adsorbs dissociatively at the same type of site (Steps 1 and 2). In Steps 3 and 4, adsorbed hydrogen atoms add sequentially across the carbonyl group. The first hydrogen addition (Step 3) forms a half-hydrogenated intermediate (KH). In Step 4, the addition of a second hydrogen atom to the half-hydrogenated intermediate forms the surface-bound alcohol (A), which then desorbs from the surface (Step 5). Vannice has employed this model to explain observed trends in vapor-phase acetone hydrogenation over Pt [24], and it is worth considering whether this scheme can capture analogous trends observed here over Ru.

Through Langmuir-Hinshelwood analysis, one can develop overall rate laws from the scheme in Table 5 (See Online Supporting Information). Doing so, H₂ adsorption can be immediately excluded as rate controlling since this scenario fails to capture apparent reaction orders over a broad range of experimental conditions. To further aid in elucidating rate controlling phenomena, we performed an H₂/D₂ switching experiment, which revealed a primary kinetic isotope effect (KIE) of approximately 3 during 2-pentanone hydrogenation (see online supporting information). This result indicates that an H-X bond is involved in the rate determining step of ketone hydrogenation, which allows us to additionally exclude ketone adsorption (Step 1) and alcohol desorption (Step 5) as rate controlling. Surface reactions are therefore the only possible rate controlling steps in this scenario. By making the assumption that the first hydrogenation step (Step 3) controls the rate of reaction (and that, relative to this step, adsorption steps are equilibrated), one predicts observable ketone orders from -1 to 1 and hydrogen orders from -0.5 to 1.5, with precise orders depending on the most abundant surface intermediate (Eq. 2).

$$r_{3+} = k_{3+} \theta_{K^*} \theta_{H^*} = \frac{k_{3+} K_1 \sqrt{K_2 P_{H_2}} P_K}{(1 + K_1 P_K + \sqrt{K_2 P_{H_2}} + \frac{K_5 P_A}{K_4 \sqrt{K_2 P_{H_2}}} + K_5 P_A)^2} \quad (2)$$

Analogously, if one assumes that the second hydrogenation step (Step 4) is rate controlling, one predicts ketone orders between -1 and 1 and hydrogen orders between 0 and 1 (Eq. 3).

$$r_{4+} = k_{4+} \theta_{KH^*} \theta_{H^*} = \frac{k_{4+} K_1 K_2 K_3 P_K P_{H_2}}{(1 + K_1 P_K + \sqrt{K_2 P_{H_2}} + K_1 \sqrt{K_2 K_3 P_K} \sqrt{P_{H_2}} + K_5 P_A)^2} \quad (3)$$

Based on the range of possible reaction orders, one concludes that our observed trends loosely agree with a single-site model and that neither surface reaction can be excluded as potentially

rate controlling. However, it is worth noting that Eq. (2) and Eq. (3) both predict maxima in the hydrogenation rate with respect to ketone partial pressure. This indicates that, for a single site model, zero-order kinetics with respect to the ketone will only be observable over a narrow partial pressure range. Since we identify no rate maximum with respect to the ketone, and we observe that saturation kinetics exist over two orders of magnitude in ketone partial pressure (Fig. 2), reconciliation with a single site model is dubious. Instead, we propose that the only way for ketone saturation kinetics to be observable alongside a half-order hydrogen dependence over such a large partial pressure range is for the rate controlling surface reaction to involve species adsorbed at two non-equivalent surface sites.

4.3 Two site model

Previous studies of acetone hydrogenation over Pt [23] and Ru [25] have invoked a two-site model to explain trends similar to those reported here. As illustrated in Table 6, this generally is presented as a scenario in which hydrogen atoms and hydrocarbons adsorb at distinct surface sites, both of which are involved in surface hydrogenation steps.

Table 6. Proposed set of elementary steps to describe ketone hydrogenation over Ru surfaces, with the non-competitive adsorption of hydrogen.

Elementary step	Surface Reaction
1.	$K + * \xrightleftharpoons{K_1} K_*$
2.	$H_2 + 2s \xrightleftharpoons{K_2} 2H_s$
3.	$K_* + H_s \xrightleftharpoons{K_3} KH_* + s$
4.	$KH_* + H_s \xrightleftharpoons{K_4} A_* + s$
5.	$A + * \xrightleftharpoons{K_5} A_*$

In this view, hydrogen binds preferentially at an ‘s’ site, whereas the ketone, half-hydrogenated intermediate, and alcohol all adsorb on ‘*’ sites. Following a Langmuir-Hinshelwood analysis (see online supporting information), we can again exclude H₂ adsorption (Step 2) as rate controlling. Furthermore, as described in the preceding section, our observation of a primary KIE during H₂/D₂ switching experiments indicates that ketone adsorption (Step 1) and alcohol desorption (Step 5) are not rate controlling. We therefore take adsorption steps to be quasi-equilibrated relative to the surface reactions, either of which may be rate determining. If the first hydrogen addition (Step 3) is controlling, Eq. (4) will describe the overall hydrogenation rate. From this model, one predicts that both ketone and hydrogen orders may range from 0 to 1.

$$r_{3+} = k_{3+} \theta_{K^*} \theta_{H_s} = \frac{k_{3+} K_1 \sqrt{K_2 P_{H_2}} P_K}{(1 + K_1 P_K + \frac{K_5 P_A}{K_4 \sqrt{K_2 P_{H_2}}} + K_5 P_A)(1 + \sqrt{K_2 P_{H_2}})} \quad (4)$$

By inspection of Eq. (4), a zero order ketone dependence and a half-order hydrogen dependence (observed reaction orders at 322K) could occur either under conditions where ‘*’ sites are saturated with the ketone and ‘s’ sites are sparsely covered with hydrogen, or under conditions where ‘*’ sites are dominated by the half-hydrogenated intermediate and ‘s’ sites are dominated by hydrogen atoms. A 0.9 order hydrogen dependence alongside a 0.4 order ketone dependence (observed reaction orders at 422K) can only result if the half-hydrogenated intermediate ($K_5 P_A / K_4 \sqrt{K_2 P_{H_2}}$) is the dominant species on ‘*’ sites and hydrogen coverage approaches zero on ‘s’ sites. Specifically, this is the only scenario in which hydrogen orders can exceed 0.5. Applying these limiting assumptions and expressing the ketone and alcohol partial pressures in terms of fractional conversion, one generates Eq. (5):

$$r_{3+} = k_{3+} \frac{K_1 K_2 K_4}{K_5} \frac{P_{H_2} P_K}{P_A} = k_{3+} \frac{K_1 K_2 K_4}{K_5} P_{H_2} \frac{(1 - X_K)}{X_K} = k' \frac{(1 - X_K)}{X_K} \quad (5)$$

In this expression, X_K is the fractional conversion of the ketone. Since hydrogen was fed in large excess and ketone conversions were maintained at differential levels, hydrogen conversion is negligible and its partial pressure can be considered constant at the inlet value and lumped into the apparent rate constant, k' . From Eq. (5), one predicts that observed site time yields will be a strong function of conversion/contact time, increasing linearly from a zero y-intercept when plotted as a function of $\frac{(1 - X_K)}{X_K}$. By inspection of Fig. 6, this trend is distinctly absent during acetone hydrogenation at 422K. Instead, we observe that the hydrogenation STY is roughly invariant with conversion. Therefore, we exclude the first hydrogen addition as a likely rate determining step in the two-site model.

Figure 6: Effect of ketone conversion on the rate of acetone hydrogenation at 442 K, 4.8 Torr acetone and 910 Torr H₂.

Analogously, by assuming that the second hydrogen addition controls the reaction rate, one arrives at the overall rate expression given in Eq. (6), which again suggests that both ketone and hydrogen orders can range from 0 to 1.

$$r_{4+} = k_{4+} \theta_{KH_s} \theta_{H_s} = \frac{k_{4+} K_1 K_2 K_3 P_K P_{H_2}}{(1 + K_1 P_K + K_1 \sqrt{K_2 K_3 P_K} \sqrt{P_{H_2}} + K_5 P_A)(1 + \sqrt{K_2 P_{H_2}})} \quad (6)$$

In this case, the zero (ketone) and half (hydrogen) reaction orders observed at low temperatures are anticipated in two scenarios—one in which ‘*’ sites are dominated by the ketone and ‘s’ sites are dominated by hydrogen atoms and another in which ‘*’ sites are dominated by the half-hydrogenated intermediate and ‘s’ sites are sparsely covered. At higher temperatures, either scenario can plausibly lead to an approximate 0.4 order ketone dependence and an approximate 0.9 order hydrogen dependence so long as the vacant site coverage becomes comparable to that of adsorbed species. Because physically realistic assumptions allow Eq. (6) to be qualitatively consistent with observed kinetic trends, we conclude that the second hydrogen addition is the most likely rate determining step.

This analysis indicates that a model involving two distinct surface sites that preferentially coordinate either hydrogen or oxygenated hydrocarbons can capture experimental trends; however, it does not establish the nature of the two sites, nor does it consider whether preferential binding of individual species at unique sites is realistic on Ru surfaces. Before proceeding further with microkinetic analysis based on the two-site model, we first consider whether there exists a sound physical basis for doing so.

4.4 Identifying potential adsorption sites on Ru surfaces

In this section, we consider the identity of possible adsorption sites and discuss whether it is realistic for adsorbates involved in ketone hydrogenation to populate two distinct categories. We limit discussion to the most thermodynamically stable Ru facet, Ru (0001) [29], which is illustrated as a 3 x 3 unit cell in Fig. 7. On this surface, there exist four distinct sites on which adsorbates may bind: top, bridge, three-fold hollow (fcc) and three-fold hollow (hcp). Top sites are so-named because they are located directly atop a Ru atom, while bridge sites comprise the intersection of two neighboring Ru atoms. Three-fold hollow (hcp) sites are found at the intersection of three Ru atoms directly above a subsurface Ru atom, whereas three-fold hollow (fcc) sites represent the analogous intersection with no Ru atom directly below.

Figure 7: Ru (0001) facet with a lattice constant of 2.71 Å with the distinct adsorption sites: 1) top, 2) bridge, 3) three-fold fcc and 4) three-fold hcp. Dashed lines indicate atoms in the second layer.

There is no reason to expect that a single adsorption site is universally preferred: a given species will bind preferentially at whichever site provides the greatest degree of energetic stabilization upon adsorption, and this will generally differ between adsorbates. For example, on Ru (0001), low-energy electron diffraction (LEED) experiments reveal that carbon monoxide adsorbs selectively at top sites [30], while oxygen atoms bind most favorably at three-fold hollow (hcp)

sites [31]. Next, we extend this discussion to surface intermediates involved in ketone hydrogenation.

4.4.1 Identifying potential adsorption sites on Ru surfaces: Hydrogen

The most straightforward case is that of hydrogen, for which surface science provides definitive resolution of adsorption phenomena. Scanning tunneling microscopy (STM) [32], high resolution electron energy loss spectroscopy (HREELS) [33] and LEED [34-37] indicate that molecular H_2 dissociates on Ru surfaces, and that the resulting hydrogen atoms bind preferentially at three-fold hollow (fcc) sites. Stable H-adsorption at top, bridge, or three-fold hollow (hcp) sites is not generally observed. Importantly, this appears independent of hydrogen coverage, suggesting that the insight can be extended to Ru surfaces under working H_2 pressures [35]. In support of experimental results, computational analyses consistently report large hydrogen binding energies at three-fold hollow (fcc) sites and conclude that these are the most likely sites for hydrogen adsorption [28, 29, 38, 39].

4.4.2 Identifying potential adsorption sites on Ru surfaces: Ketone

Two ketone adsorption modes have been proposed on Group VIII metals [40, 41]; both are illustrated in Fig. 8. First, carbonyl groups can adsorb end-on through interactions between surface metal atoms and an oxygen lone pair. This binding mode is designated as $\eta_1(O)$. Second, the carbonyl can bind side-on through interactions between metal surface sites and both the carbon and oxygen of the carbonyl group. This binding mode is designated as $\eta_2(C,O)$, and it will generally require two metal sites [40, 41]. Experimentally, both modes have been identified on Ru (0001) through electron energy loss spectroscopy (EELS) [41]. Density Functional Theory (DFT) calculations have also shown that $\eta_1(O)$ and $\eta_2(C,O)$ are the preferred modes of acetone

adsorption on Ru, while 2-butanone preferentially binds in the $\eta_1(\text{O})$ configuration [28]. To define precise site requirements, ketones bound as $\eta_1(\text{O})$ species will be located at top sites, while those in the $\eta_2(\text{C},\text{O})$ configuration occupy a neighboring pair of top and bridge sites.

Figure 8: Spectroscopically observed adsorption modes of acetone on a clean Ru (0001) surface [41]

4.4.3 Identifying potential adsorption sites on Ru surfaces: Half-hydrogenated intermediate

In order to discuss the adsorption mode of the half-hydrogenated intermediate (KH), it is necessary to first establish its chemical identity. Depending on the sequence of hydrogen addition to the surface-bound ketone in the Horiuti-Polanyi scheme, the half-hydrogenated intermediate (product of Step 3, Table 6) will be either an alkoxy or a hydroxyalkyl. The former will be observed if the first hydrogen atom adds to the carbonyl carbon, while the latter will be observed if the first hydrogen atom adds to the carbonyl oxygen. As illustrated in Fig. 9, each species will adopt a distinct surface configuration and thus have unique site requirements. Specifically, an alkoxy will bind at a single adsorption site through its oxygen atom [40], while a hydroxyalkyl will form a di-sigma bond, requiring two neighboring sites [28].

Figure 9: Expected adsorption modes of alkoxy and hydroxyalkyl intermediates on the surface

The precise nature of the half-hydrogenated intermediate comprises a long-standing debate, which has been examined using both experimental and computational methods; here, we summarize the general consensus of the literature. Experimental studies of alcohol dehydrogenation overwhelmingly support alkoxy formation [40, 42-47]. To date, there is no spectroscopic evidence of hydroxyalkyl species existing as intermediates between the ketone and the alcohol in the hydrogenation/dehydrogenation landscape on metal surfaces. Similarly, DFT studies of ketone hydrogenation on Ru [12, 28] surfaces consistently report that—relative to the hydroxyalkyl species—alkoxy binding energies are large and the kinetic barrier to their formation (from the ketone) is small. In general, they conclude that the half-hydrogenated intermediate (KH) is most likely an alkoxy. Given the strong experimental and theoretical evidence, we extend this conclusion to the remainder of our analysis and disregard the hydroxyalkyl species as an abundant surface intermediate in this system.

On Ru (0001) surfaces, alkoxy binding has been considered primarily through computational and spectroscopic analysis of methoxy species formed during methanol adsorption. Specifically,

perturbations in the vibrational spectra of adsorbed methoxy species are taken to reflect the geometric orientation of the methoxy on the surface. From this, one can obtain insight into the binding mode and the likely adsorption site. Computational analysis suggests that alkoxy species adsorbed in either type of three-fold hollow site will have an upright geometry, i.e., their C-O bond is orthogonal to the Ru surface. In contrast, if alkoxies bind at top and bridge sites, their C-O bond is tilted relative to the Ru surface [48]. DFT results, which are generally reported at low coverage, consistently reveal that methoxy species bind most favorably at three-fold hollow (hcp) sites [48-50] and possibly both three-fold hollow (hcp) and (fcc) sites [48]. Experimentally, methoxies formed at low coverages bind normal to the metal surface, which is indicative of adsorption at either type of three-fold hollow site [48, 51] and thus consistent with DFT predictions. At higher coverages, methoxies adopt tilted geometries, indicating a shift from three-fold hollow sites to top or bridging sites [51, 52]. Therefore, it appears that alkoxy species bind at multiple adsorption sites, and that their preferred mode is coverage dependent. In particular, evidence suggests that alkoxies—at the high coverages expected under working conditions—may be bound at top and bridge sites.

4.4.4 Identifying potential adsorption sites on Ru surfaces: Alcohol

Finally, considering the alcohol product, experimental studies have not identified its preferred adsorption mode on Ru surfaces. Computational studies, however, consistently find top sites to be the most favorable location for alcohol adsorption on Ru (0001) [12, 28, 49].

From the above discussion, it is reasonable to conclude that hydrogen atoms bind most favorably at three-fold hollow (fcc) sites. Oxygenate binding, particularly in the case of the alkoxy, is less certain; however, it appears that there may be a slight preference toward adsorption at top or

bridge sites under working conditions. It therefore stands to reason that ketone hydrogenation on Ru can be cast in terms of elementary processes occurring at two distinct surface sites, particularly since this scenario reconciles with observed kinetic trends.

4.5 Microkinetic analysis

The set of elementary steps given in Table 6 have a sound physical basis and reconcile with experimentally observed hydrogenation rates. Full kinetic parameterization of these elementary reactions is powerful in that it allows one to develop a predictive model of surface coverage and ketone hydrogenation rates under a wide range of experimental conditions. Unfortunately, free energies of activation are generally not known *a priori*, nor are they easily estimated. Furthermore, because we have measured here only macroscopic production rates of hydrogenation products, we lack the ability to (meaningfully) resolve and/or regress the complete set of kinetic parameters from our experimental data. To reduce the size of the necessary parameter set, we invoke a limiting assumption: that the second surface hydrogen addition (Step 4, Table 6) always controls the rate of ketone hydrogenation and that, relative to this step, all other processes are equilibrated. This results in the overall rate expression given in Eq. (6), which we have already demonstrated is qualitatively consistent with experimental data. In doing so, we reduce the burden of estimating activation free energies to a single quantity (k_{4+}). Instead, the majority of parameters in the overall rate expression comprise reaction free energies (K_i), many of which can be independently estimated from experimental data and published correlations.

We assume that both activation and reaction free energies may vary with the nature of the ketone being hydrogenated, formally requiring that the model be parameterized in triplicate to fully capture trends in acetone, 2-butanone, and 2-pentanone hydrogenation. Where possible, we rely

on correlations to reduce the need for independent parameter estimation. Our approach to doing so is detailed in sections 4.5.1 to 4.5.4.

4.5.1 Microkinetic analysis: gas phase thermochemistry

Enthalpies and entropies for all surface species are necessary for calculating elementary reaction free energies for each step in Table 6. Here, we reference each surface species to its gas phase analog; accordingly, we begin by introducing Table 7, which summarizes tabulated and estimated thermodynamic data for stable gas phase species (H_2 , 2-ketones, 2-alcohols) and gas phase analogs of surface intermediates (hydrogen atoms, alkoxies/alkoxides). Standard values of gas phase molecules are corrected to reaction temperature using published heat capacities, which are linear in temperature over our range of experimental conditions and thus well-described by the truncated expression given in Eq. (7). Parameters a and b were obtained in house by regression of published heat capacity data.

$$C_p = a + bT \quad (7)$$

Table 7. Summary of energetics of gas phase species.

	ΔH_f^0 (g) (kJ mol ⁻¹)	S^0 (g) (J mol ⁻¹ K ⁻¹)	a (J mol ⁻¹ K ⁻¹)	b (J mol ⁻¹ K ⁻²)
Acetone	-217.4	295.4	26.3	0.16
2-butanone	-238.5	338.2	37.2	0.22
2-pentanone	-259.1	378.2	38.2	0.29
Isopropanol	-272.3	309.8	26.3	0.21
2-butanol	-293.1	355.4	40.0	0.25
2-pentanol	-314.7	397.1	59.5	0.28
H_2	0	130.7	29.0	-
H	218.0	114.7	20.8	-
H^+	1534.1	108.8	20.8	-
Isopropoxy/propoxide	-47.3 [†]	293.0 [†]	-	-
2-butoxy/butoxide	-68.1 [†]	338.6 [†]	-	-
2-pentoxy/pentoxide	-89.7 [†]	380.3 [†]	-	-

[†]Estimated quantity

Tabulated gas-phase data are not available for gas-phase analogs of surface alkoxies; however, their entropies and enthalpies can be estimated based on the energetics of alcohol dissociation. The entropy change of alcohol deprotonation to form an alkoxide anion and a proton in the gas phase has been measured at $92 \text{ J mol}^{-1} \text{ K}^{-1}$, which is independent of the alcohol's identity and chain length [53]. From this quantity, one can calculate the entropy of the gas-phase alkoxide anion (Equation 8). Because alkoxy radicals and alkoxide anions will have similar masses and molecular structures, we take this value as a reasonable approximation for entropy of the gas-phase alkoxy.

$$S_{\text{alkoxide (g)}} = S_{\text{alcohol (g)}} + \Delta S_{\text{diss (g)}} - S_{\text{H}^+ \text{ (g)}} \quad (8)$$

Here, $S_{\text{H}^+ \text{ (g)}}$ is the entropy of a proton in the gas phase, which is estimated to be $108.8 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298 K [54] and $\Delta S_{\text{diss (g)}}$ is the entropy of alcohol deprotonation, which we assume to be temperature invariant. In this manner, we estimate the entropy of the alkoxide to be lower than that of the alcohol by $\approx 17 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298 K.

Analogously (Eq. 9), one can calculate the enthalpy of the gas-phase alkoxy radical from the homolytic bond dissociation energy (BDE) of the RO-H group, which is also not expected to vary with chain length [24, 55, 56].

$$\Delta H_{f, \text{alkoxy (g)}} = \Delta H_{f, \text{alcohol (g)}} + \text{BDE}_{\text{RO-H}} - \Delta H_{f, \text{H (g)}} \quad (9)$$

Here, we have taken 443 kJ mol^{-1} as the BDE of any secondary alcohol. This value represents the average BDE of isopropanol measured using multiple experimental techniques [55], and we explicitly assume that it is temperature-invariant. Estimated gas-phase entropies (Eq. 8) and enthalpies (Eq. 9) for linear $\text{C}_3 - \text{C}_5$ alkoxy species are summarized at 298 K alongside stable gas

phase molecules in Table 7. Because alkoxy thermochemistry is always referenced to that of the gas-phase alcohol in our calculations, temperature corrections are included in the enthalpy and entropy of the alcohol; as such, we have not estimated heat capacities for the alkoxy species.

4.5.2 Microkinetic analysis: adsorption energetics

Enthalpies and entropies for surface species are calculated by adjusting gas-phase quantities (Table 7) by their enthalpies and entropies of adsorption on Ru surfaces (Eq. 10 and 11), both of which must be estimated.

$$S_{j*} = S_{j(g)} + \Delta S_{j\ ads} \quad (10)$$

$$H_{j*} = \Delta H_{f,j(g)} + \Delta H_{j\ ads} \quad (11)$$

Adsorption entropies

Previously reported kinetic studies involving dissociative H₂ adsorption on Ru [57, 58], Pt [59, 60], Fe [61-63] and Cu [64] surfaces indicate that, on average, molecular H₂ loses approximately 90% of its gas phase entropy upon dissociative adsorption, which suggests a complete loss of translational entropy for molecular hydrogen. Accordingly, we estimate the entropy change for dissociative hydrogen adsorption (ΔS_2) to be -117.5 J mol⁻¹ K⁻¹ at 298 K. From this value and thermodynamic data in Table 7, one can calculate the entropy of a surface hydrogen atom ($S_{H,s} = 6.6$ J mol⁻¹ K⁻¹) and the adsorption entropy for a gas-phase hydrogen atom ($\Delta S_{ads,H} = -108.1$ J mol⁻¹ K⁻¹) at 298 K.

For all other species, which are taken to adsorb molecularly, adsorption entropies are calculated using the relationship proposed by Campbell for molecules with standard gas phase entropy below 60R [65]:

$$\Delta S_{ads} = -(0.3S_{gas} + 0.7S_{trans,1D}) \quad (12)$$

In this correlation, S_{gas} is the total entropy of the molecule in the gas phase and $S_{trans,1D}$ is the entropy contribution of 1 degree of translational freedom in the gas phase. The latter is calculated using the Sackur-Tetrode equation [65]:

$$S_{1D,trans} = \frac{1}{3} \left\{ 18.6R + R \ln \left[\left(\frac{m}{m_{Ar}} \right)^{3/2} \left(\frac{T}{298} \right)^{5/2} \right] \right\} \quad (13)$$

Here, m and m_{Ar} are, respectively, the molar masses of the species of interest and Argon, and R is the universal gas constant. Parameterized as described in this section, adsorption entropies for all species are constrained such that they are always negative and never exceed the total entropy of the gas phase species, which is consistent with thermodynamic expectations.

Adsorption enthalpies

Based on experimental (TPD) and computational (DFT) analysis, one can estimate that the binding energy of a hydrogen atom on a clean Ru surface is roughly 270 kJ mol⁻¹ [29, 66]. However, heats of dissociative hydrogen adsorption on Ru are a strong function of both coverage [67] and Ru particle size [68]; therefore, it is difficult to assign a specific hydrogen binding energy under the conditions of our study. Accordingly, we take 270 kJ mol⁻¹ as an initial estimate and aim to regress a hydrogen binding energy (BE_H) that permits reconciliation with experimental data. To fully specify the use of the hydrogen binding energy in our calculations,

we take its value to be equal to the negative heat of adsorption of a gas-phase hydrogen atom onto a Ru surface.

$$\Delta H_H = -BE_H \quad (14)$$

With respect to ketone binding, Anton reported the desorption energy of acetone from a bare Ru (0001) surface to be $54.4 \pm 10.5 \text{ kJ mol}^{-1}$ using temperature programmed desorption (TPD) [41]. Here, we take this value as equal to the negative of the enthalpy of acetone chemisorption, which invokes the assumption that acetone adsorption is non-activated. Analogous data for 2-butanone and 2-pentanone have not been reported; therefore, we employ a generalized correlation to estimate their heats of adsorption relative to that of acetone. In developing this model, we assume that the primary interaction between the ketone adsorbate and the Ru surface is through the carbonyl oxygen and that the strength of this interaction (i.e., the carbonyl binding energy on Ru) is identical for acetone, 2-butanone, and 2-pentanone. Differences in heats of adsorption are therefore entirely attributed to the effect of varying carbon chain length.

Typically, as the length of the carbon chain increases for a given class of functional molecules, adsorption becomes more exothermic. This is attributed to van der Waals interactions between the metal surface and methylene groups, which increase with chain length and stabilize adsorption relative to the primary carbonyl-metal interaction [69, 70]. In general, heats of adsorption scale linearly with the length of the primary carbon chain. For example, desorption energies for n-alkanes over Ru [71], Pt [69, 70], Au [72] and Cu [69, 70, 73] surfaces gain 5 – 10 kJ mol^{-1} for each additional carbon atom in the alkyl chain. Similarly, Sexton & Rendulic have reported that each additional carbon in the longest alkyl side chain of $\text{C}_1\text{-C}_4$ alcohols and $\text{C}_1\text{-C}_5$ ethers stabilizes their adsorption on Pt by 5.4 kJ mol^{-1} [74]. It therefore stands to reason that

enthalpies of ketone adsorption can be described as a linear function of chain length. Because the enthalpy of acetone adsorption on Ru has been experimentally estimated, we reference all ketone heats of adsorption to that of acetone in this model. This provides a reasonable and convenient initial parameterization of ketone adsorption enthalpies in this system:

$$\Delta H_{ads,i} = \Delta H_{ads,Acetone} - \beta_K * (N_s - 2) \quad (15)$$

Here, $\Delta H_{ads,Acetone}$ represents the enthalpy of acetone chemisorption, β_K represents the enthalpic stabilization conferred by one additional carbon atom in the main alkyl chain, and N_s is the number of carbon atoms in the longest alkyl side chain. Using Sexton's convention [74], the longest alkyl side chains in acetone, 2-butanone, and 2-pentanone have, respectively, two, three, and four carbon atoms. $\Delta H_{ads,Acetone}$ is initially set at the experimentally reported value, -54.4 kJ mol⁻¹, and β_K is taken to be 5.8 kJ mol⁻¹ Carbon⁻¹, which has been previously reported to capture the trend in alkane chemisorption on Ru surfaces [69, 71]. At this stage, we view both quantities as potentially adjustable parameters.

To establish heats of alkoxy chemisorption on Ru, we employ an analogous correlation to that developed in Eq. (15). In doing so, it is helpful to define a quantifiable “anchor point” as we have done above using the heat of adsorption for acetone. Since the energetics of alkoxy binding have not been experimentally measured on Ru, we estimate their values by extension of reported trends in hydroxy/alkoxy binding on both Ru and Pt surfaces. Specifically, Campbell has proposed that, on a variety of metal surfaces, there is a constant offset between hydroxy binding energies (BE_{OH}) and alkoxy binding energies (BE_{Alkoxy}) [75-77]. Accordingly, for Ru and Pt, one can develop Eq. (16):

$$\left(BE_{OH} - BE_{Alkoxy} \right)_{Ru} = \left(BE_{OH} - BE_{Alkoxy} \right)_{Pt} \quad (16)$$

On Pt (111), Campbell estimated that the methoxy binding energy is $\approx 60 \text{ kJ mol}^{-1}$ smaller than the analogous hydroxy binding energy [75, 78]. Eq. (16) therefore suggests that, on Ru, the methoxy binding energy will also be smaller than the hydroxy binding energy by $\approx 60 \text{ kJ mol}^{-1}$. Using DFT methods, Heyden estimated a hydroxy binding energy of $336.8 \text{ kJ mol}^{-1}$ on Ru (0001) [49]. Accordingly, we estimate the methoxy binding energy on Ru (0001) to be $276.8 \text{ kJ mol}^{-1}$. As described above for ketone adsorption, we take this quantity as equal to the negative enthalpy of methoxy chemisorption such that $\Delta H_{ads, methoxy} = -276.8 \text{ kJ mol}^{-1}$. With this established, heats of alkoxy chemisorption are estimated relative to that of methoxy as a function of the length of the longest alkyl side chain in the adsorbate (N_s), where methoxy has an alkyl chain length of one:

$$\Delta H_{ads,i} = \Delta H_{ads, methoxy} - \beta_{KH} * (N_s - 1) \quad (17)$$

As in the case of ketone chemisorption, β_{KH} is the parameter describing the amount of enthalpic stabilization per additional carbon atom in the longest alkyl side chain. Since stabilization is again expected to come from increasing van der Waals interactions with each methylene group in the longest alkyl side chain, its value is taken as equal to that estimated for chain length stabilization in adsorbed ketones, $5.8 \text{ kJ mol}^{-1} \text{ Carbon}^{-1}$.

Alcohol heats of adsorption have not been reported on Ru; therefore, we relate their values to ketone adsorption enthalpies (Eq. 15) based on observed trends in experimental literature. Specifically, on Cu[70] and Pt[70, 79-81], isopropanol adsorption is roughly 10% more

exothermic than acetone adsorption. We thus assume the same trend holds for alcohol adsorption on Ru and calculate their adsorption enthalpies using Eq. (18):

$$\Delta H_{ads,OH,i} = 1.10 \cdot \Delta H_{ads,K,i} \quad (18)$$

With respect to thermochemistry, we have defined all necessary surface enthalpies and entropies using tabulated data and reasonable correlations. Accordingly, reaction enthalpies, reaction entropies, reaction free energies, and equilibrium constants can be computed for each elementary step of the scheme in Table 6 using Eq. (19) – (22).

$$\Delta H_i = \sum_j \nu_{i,j} \cdot H_j \quad (19)$$

$$\Delta S_i = \sum_j \nu_{i,j} \cdot S_j \quad (20)$$

$$\Delta G_i = \Delta H_i - T \cdot \Delta S_i \quad (21)$$

$$K_i = \exp\left(\frac{-\Delta G_i}{R \cdot T}\right) \quad (22)$$

Built into these reaction thermochemistries and equilibrium constants are five potentially adjustable parameters for which we have made reasonable initial guesses: The hydrogen binding energy on Ru (BE_H), the heat of acetone chemisorption on Ru ($\Delta H_{\text{ads,acetone}}$), the heat of methoxy chemisorption on Ru ($\Delta H_{\text{ads,methoxy}}$), and the variation in adsorption enthalpy with the length of the alkyl side chain in the ketone (β_K) or the alkoxy (β_KH).

4.5.3 Microkinetic analysis: kinetics of the rate controlling step

The remaining undefined parameters are forward pre-exponential factors and energy barriers for the rate determining step, which we take to be the addition of a hydrogen atom to a surface alkoxy (Step 4, Table 6). Per Arrhenius, one may define the forward rate constant in terms of a pre-exponential factor (A_{4+}) and an activation barrier ($E_{a,4+}$).

$$k_{4+} = A_{4+} e^{-E_{a,4+}/RT} \quad (23)$$

Since this model considers hydrogenation of three separate ketones, it is ostensibly necessary to estimate six activation parameters: three barriers and three pre-exponential factors. Fortunately, the size of this parameter set can be reduced using Brønsted–Evans–Polanyi (BEP) linear scaling relations, which link the activation barrier for a given step to its reaction enthalpy. Of particular relevance, Sautet has parameterized a BEP relation governing the barrier of O-H dissociation in surface-bound alcohols to form their respective alkoxy [82]. Importantly, this is the reverse of the apparent rate controlling step during ketone hydrogenation—addition of a hydrogen atom to the oxygen atom of a surface bound alkoxy. Accordingly, we recast his correlation in the associative direction (Eq. 24), where the heat of reaction (ΔH_4) is defined, per Step 4 of our *hydrogenation* reaction sequence, as proceeding from the surface bound alkoxy to the surface bound alcohol.

$$E_{a,4+} = (1-\alpha)\Delta H_4 + \beta \quad (24)$$

Here, the value of α reflects the earliness of the transition state and β is a reference activation barrier. From DFT analysis of alcohol dissociation on multiple metal surfaces, Sautet has estimated α and β to be 0.11 and 0.83 eV respectively, and we fix their values here for the remainder of our analysis [82]. This correlation allows us to compute ketone-specific barriers

from elementary reaction enthalpies, which have been defined in the preceding section; therefore, its use eliminates the need for independent estimation of activation barriers in this analysis.

At present, we have no reliable correlation permitting analogous estimation of elementary pre-exponential factors for each ketone. As such, separate pre-factors are specified for the hydrogenation of each ketone, and we aim to regress their values during model reconciliation with experimental data. As shown in Eq. (25), pre-exponential factors can be related to the entropy of activation ($\Delta S_{4+}^\ddagger$) for a given elementary step [83]. We use this parameterization and work with activation entropies for the remainder of our analysis.

$$A_{4+} = e \frac{k_b T}{h} e^{\Delta S_{4+}^\ddagger / R} \quad (25)$$

To provide an order-of-magnitude initial estimate for each pre-factor, we assume activation entropies for step 4 ($\Delta S_{4+}^\ddagger$) are near zero regardless of the ketone undergoing hydrogenation, which gives a pre-exponential factor of roughly 10^{13} s^{-1} for the rate controlling step in acetone, 2-butanone, and 2-pentanone hydrogenation.

Kinetic parameterization of the rate controlling step for each ketone thus adds three potentially variable activation entropies to the set of five uncertain quantities described in thermodynamic parameterization of the model. In total, the microkinetic model developed here includes eight potentially adjustable parameters. They are identified along with their initial estimates in Table 8.

Table 8. Summary of potentially adjustable parameters and their initial estimates.

Adjustable Parameter	Initial estimate	Units
BE_H	270	kJ mol^{-1}
$\Delta \text{H}_{\text{ads,acetone}}$	-54.4	kJ mol^{-1}

$\Delta H_{\text{ads, methoxy}}$	-276.8	kJ mol^{-1}
β_K	5.8	$\text{kJ mol}^{-1} \text{ Carbon}^{-1}$
β_{KH}	5.8	$\text{kJ mol}^{-1} \text{ Carbon}^{-1}$
$\Delta S_{4, \text{acetone}}^\ddagger$	0	$\text{J mol}^{-1} \text{ K}^{-1}$
$\Delta S_{4, \text{2-butanone}}^\ddagger$	0	$\text{J mol}^{-1} \text{ K}^{-1}$
$\Delta S_{4, \text{2-pentanone}}^\ddagger$	0	$\text{J mol}^{-1} \text{ K}^{-1}$

4.5.4 Microkinetic analysis: regression results

Prior to final optimization, the initial set of eight adjustable parameters was reduced to five through sensitivity analysis and preliminary regression. With our initial parameter set, the rate of ketone hydrogenation is insensitive to the value of β_K , which captures the effect of chain length on stabilizing ketone adsorption on Ru (Eq. 15). Accordingly, its value was fixed at the initial estimate of $5.8 \text{ kJ mol}^{-1} \text{ Carbon}^{-1}$. Hydrogenation rates were moderately sensitive to the analogous quantity governing chain length stabilization of alkoxies, β_{KH} (Eq. 17); however, its regressed value ($5.5 \pm 0.5 \text{ kJ mol}^{-1} \text{ Carbon}^{-1}$) was statistically indistinguishable from the initial estimate. As in the case of ketone adsorption, β_{KH} was fixed at $5.8 \text{ kJ mol}^{-1} \text{ Carbon}^{-1}$. Whether in describing ketone binding or alkoxy binding, β_i most likely reflects increasing van der Waals stabilization upon increasing the length of the carbon chain. In either case, interactions between methylene groups with the Ru surface should be similar, and it is not surprising that we are unable to resolve a difference in the influence of chain length on their adsorption enthalpies from regression of kinetic data. Finally, the regressed adsorption enthalpy for the methoxy was found to vary less than 1% from the initial estimate. Its adsorption enthalpy was therefore fixed at the initial estimate of $-276.8 \text{ kJ mol}^{-1}$. The rate of hydrogenation was sensitive to the remaining five parameters, and their regressed values varied substantially from initial guesses. Regressed parameters are presented with 95% confidence intervals in Table 9. Thermodynamic consistency of the model with the regressed parameter set was confirmed by ensuring that elementary

reaction free energies weighted by their stoichiometric numbers sum to the overall gas phase free energy for ketone hydrogenation.

Table 9. Summary of optimized parameters found from the regression of experimental data. Uncertainty in optimized values was estimated at a 95% confidence level.

Parameter	Optimized value	Units
BE_H	233.2 ± 2.8	kJ mol^{-1}
$\Delta H_{\text{ads,acetone}}$	-80.8 ± 1.4	kJ mol^{-1}
$\Delta H_{\text{ads,methoxy}}$	$-276.8^\dagger$	kJ mol^{-1}
β_K	$5.8^\dagger$	$\text{kJ mol}^{-1} \text{Carbon}^{-1}$
β_{KH}	$5.8^\dagger$	$\text{kJ mol}^{-1} \text{Carbon}^{-1}$
$\Delta S_{4+, \text{acetone}}$	-44.1 ± 3.5	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta S_{4+, 2\text{-butanone}}$	-45.9 ± 3.9	$\text{J mol}^{-1} \text{K}^{-1}$
$\Delta S_{4+, 2\text{-pentanone}}$	-53.4 ± 3.8	$\text{J mol}^{-1} \text{K}^{-1}$

[†]Parameter not varied during optimization.

With the parameter set summarized in Table 9, the kinetic model captures observed trends in the hydrogenation of $C_3 - C_5$ ketones over a broad range of temperatures and partial pressures. This is illustrated at a high level by the parity plot in Fig. 10, which includes the entire experimental data set collected in this study. Although we did not experimentally determine apparent kinetic parameters for 2-butanone and 2-pentanone hydrogenation at elevated temperatures as we did with acetone, we did obtain hydrogenation rates for the longer-chain ketones over reasonable temperature ranges (303 – 360K for 2-butanone, 303K – 418K for 2-pentanone). As shown in Figure 10, hydrogenation rates are adequately described by the model for all ketones under all experimental conditions, suggesting the model developed here is universally applicable for ketone hydrogenation. Next, we discuss whether optimal model parameters are physically realistic and connect them with experimental observations.

Figure 10: Comparison of predicted to experimentally measured STY of ketone hydrogenation for (○) 2-pentanone, (□) 2-butanone and (Δ) acetone. Reaction conditions were varied across temperatures of 303-456 K, 0.3 - 30 Torr of ketone and 75 - 910 Torr of H₂.

The binding energy of a hydrogen atom is estimated to be $233.2 \pm 2.8 \text{ kJ mol}^{-1}$, which is substantially lower than our initial value of 270 kJ mol^{-1} . Based on the regressed binding energy, we calculate the enthalpy of dissociative H₂ adsorption on Ru (ΔH_2 , 298K) to be $-30.4 \text{ kJ mol}^{-1}$ under reaction conditions. In contrast, our initially estimated hydrogen binding energy suggests an adsorption enthalpy of -100 kJ mol^{-1} , which is generally consistent with microcalorimetry data reported at low hydrogen coverages [66]. As hydrogen pressures and coverages increase, H₂ chemisorption becomes less exothermic, reportedly decreasing to anywhere from -50 kJ mol^{-1} to -35 kJ mol^{-1} on Ru (0001) depending on the hydrogen coverage [67, 84]. On supported catalysts, King has reported that the enthalpy of H₂ chemisorption on a 4% Ru/SiO₂ catalyst decreases to -43 kJ mol^{-1} at a fractional hydrogen coverage of 0.4 [85] and further to -20 to -30 kJ mol^{-1} as the surface approaches hydrogen saturation [86]. In addition, the presence of co-adsorbates will generally decrease hydrogen binding energies. For example, the enthalpy of H₂ adsorption on Ru (0001) decreases to below -38 kJ mol^{-1} on an oxygen pre-covered surface [41]. We therefore view the relatively small H-binding energy and heat of chemisorption in the optimal parameter

set as a reasonable consequence of repulsive lateral interactions due to elevated coverages of H_2 and other adsorbates under working conditions.

The regressed enthalpy of acetone adsorption ($-80.8 \pm 1.4 \text{ kJ mol}^{-1}$) stands to reason given the relative oxophilicity and substantial oxygen binding energy of Ru. That stated, this heat of adsorption is significantly larger than our initial estimate, which was inferred from TPD experiments ($-54.4 \pm 10.5 \text{ kJ mol}^{-1}$) on a bare Ru (0001) surface. A possible source of the discrepancy is the analysis of TPD data, which used a first-order Redhead equation and assumed a desorption pre-exponential factor of 10^{13} s^{-1} . Desorption always occurs with a substantial gain in entropy, and its activation entropies are often substantially greater than zero. This suggests that a desorption pre-factors of 10^{13} s^{-1} may be a considerable underestimate, leading one to infer an artificially low desorption energy through conventional TPD analysis [65, 78, 87].

With respect to the methoxy binding enthalpy, we observe that kinetic data are well described using the initial estimate of $-276.8 \text{ kJ mol}^{-1}$, and further refinement was unnecessary. The value agrees well with multiple DFT estimates for the binding energy of methoxy on Ru (0001). Specifically, Heyden has reported a methoxy adsorption enthalpy of -268 kJ mol^{-1} [49] and Neurock has reported a value of -259 kJ mol^{-1} [28], both of which are within 10% of our estimate.

Elementary activation barriers for the rate controlling step (E_{A4+}) were computed from reaction enthalpies using the BEP relation given in Eq. (24). They are found to be statistically indistinguishable at 65.8, 65.3 and 65.8 kJ mol^{-1} for acetone, 2-butanone, and 2-pentanone, respectively. The lack of variation in regressed elementary barriers is not surprising: surface species in this system were referenced to gas phase analogs; gas phase alkoxy enthalpies were

computed using a single alcohol bond dissociation energy ($\text{BDE}_{\text{OH}} = 443 \text{ kJ mol}^{-1}$); and both ketone and alkoxy binding energies were parameterized to vary identically with chain length ($\beta_{\text{K}} = \beta_{\text{KH}} = 5.8 \text{ kJ mol}^{-1} \text{ Carbon}^{-1}$). Accordingly, the elementary reaction enthalpy for the addition of a hydrogen atom to a surface-bound alkoxy (Step 4) is nearly identical for every ketone ($\Delta H_4 \approx -16.1 \text{ kJ mol}^{-1}$), with minor variations attributed to differences in gas-phase heat capacities. Because we have coupled reaction and activation energies through a BEP relation, this leads to nearly identical elementary barriers for the rate controlling step in each ketone hydrogenation. This agrees with the observation that computationally-derived barriers for hydrogenation of surface alkoxies are invariant with chain length during the reduction of C_1 - C_4 aldehydes and ketones over Ru (0001) [28].

Regressed activation entropies were estimated for each ketone (Table 9), all of which are substantially negative, indicating a relatively tight transition state. Values cluster around $-48 \text{ J mol}^{-1} \text{ K}^{-1}$, which translates to a pre-exponential factor of $\sim 10^{11} \text{ s}^{-1}$ for each ketone and is reasonable for a bimolecular surface reaction. Although there is statistical overlap among our three regressed activation entropies, we do notice a slight trend in the magnitude of the pre-factor with the chain length of the ketone. Specifically, the activation entropy becomes more negative with the length of the main alkyl chain in the ketone, resulting in a decrease in pre-exponential factors as one goes from acetone ($1.3 \times 10^{11} \text{ s}^{-1}$) to 2-butanone ($1.2 \times 10^{11} \text{ s}^{-1}$) to 2-pentanone ($4.3 \times 10^{10} \text{ s}^{-1}$). The relative magnitude of the pre-factors mirrors the trend in observed STYs for the three ketones (Table 2), indicating that our model has primarily attributed the decrease in STY with chain length to increasingly unfavorable activation entropies in the elementary hydrogenation of isopropoxide, butoxide, and pentoxide surface species. While this is a possible explanation, it is not immediately apparent why the activation entropy for a class of analogous

chemical reactions should necessarily scale with chain length. An alternate possibility is that our model fails to capture differences in the number of sites required for adsorption of C₃, C₄, and C₅ hydrocarbons. Considering that the atomic and molecular diameter of Ru and acetone are almost identical (~2.7 Å), one might assume that a single acetone monolayer realistically corresponds to one adsorbed acetone molecule per surface Ru atom. However, 2-pentanone is substantially larger (5.1 Å), and its adsorption should lead to an inherently more crowded surface and a lower monolayer coverage than that of acetone. Practically speaking, larger molecules may impose additional “site blocking” interactions that lead to fewer effective sites for 2-pentanone hydrogenation than there are for acetone hydrogenation. Both our experimental STYs and our model assume site accessibility is independent of chain length. If accessible sites do vary with the length of the ketone, then they are likely over-counted by CO chemisorption, which would lead to lower apparent STYs for the larger ketones.

4.5.5 Microkinetic analysis: simulation results and comparison to experimental data

In addition to the elementary parameter estimates described in the preceding section, a rigorous interpretation of our apparent kinetic trends requires quantification of surface coverages under reaction conditions. Accordingly, Fig. 11 presents anticipated surface coverages obtained with the optimized parameter set by assuming that steps 1, 2, 3, and 5 (Table 6) are equilibrated at a given set of reaction conditions. Data are presented for acetone (Fig. 11a), 2-butanone (Fig. 11b), and 2-pentanone (Fig. 11c).

Figure 11: Predicted coverages of ketone (Δ), alkoxy ($\circ$), hydrogen ($\diamond$) and vacant '*' sites (*) from 303-456 K at fixed partial pressures of 4.8 Torr ketone and 910 Torr H_2 for a) acetone, b) 2-butanone, and c) 2-pentanone hydrogenation. Note that hydrocarbon species are assumed to bind at '*' sites and hydrogen atoms bind at 's' sites.

From simulated coverages, several trends are apparent. First, independent of the ketone and throughout our temperature range, there are generally few vacancies in the '*' site balance; rather, these sites are dominated by the alkoxy intermediate. In the range of 300 – 380 K, θ_{KH} ranges from 0.9 – 1.0, indicating an alkoxy saturated surface. As temperatures increase beyond 380 K, the alkoxy coverage decreases from roughly 90% to roughly 40% as coverages of both the ketone and vacant sites increase, relative to the alkoxy, with reaction temperature. Similarly, kinetic Monte-Carlo simulations of carbonyl reduction on Ru (0001) have found the alkoxy coverage to be dominant, with a decreasing trend as temperature increases [28]. In contrast, hydrogen atoms appear to sparsely cover 's' sites. At low temperatures (300 – 360 K), hydrogen coverages vary from 10% to 30%, whereas at high temperatures, 's' sites appear to be predominately vacant. With these coverage trends established, interpretation of apparent reaction orders and kinetic barriers is straightforward. Table 10 summarizes experimentally observed and model-predicted values.

Table 10. Comparison of experimentally measured and predicted apparent reaction kinetics for all ketones

Ketone	STY (s ⁻¹) ^a		E _{a,apparent} (kJ mol ⁻¹) ^a		Ketone reaction order		H ₂ reaction order	
	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted
322 K								
2-pentanone	0.14	0.16	49.5	51.1	0.01	0	0.52	0.44
2-butanone	0.33	0.34	51.8	50.8	-0.01	0	0.57	0.46
Acetone	0.37	0.36	50.1	50.6	0.03	0	0.48	0.46
442 K								
Acetone	36.7	36.6	17.7	15.2	0.4	0.38	0.92	0.99

a – reaction conditions 4.8 Torr ketone, 910 Torr H₂

By inspection of the overall rate expression (Eq. 6), one observes that low temperature reaction orders ($n_{H_2} \approx 0.5$, $n_K \approx 0$ at 322K) reconcile with the low temperature coverage regime, where alkoxies dominate ‘*’ sites and ‘s’ sites are sparsely covered by hydrogen. At high temperatures, the alkoxy coverage decreases substantially, causing the observed increase in apparent reaction orders (e.g., $n_{H_2} \approx 0.9$, $n_K \approx 0.4$ for acetone hydrogenation at 422K).

In order to interpret trends in apparent activation energies, we derive Eq. (27),[83] which specifies the complex functional dependence of the experimentally observable barrier on elementary activation energies, elementary reaction enthalpies, and surface coverages on both ‘*’ and ‘s’ sites (Eq. 27).

$$E_{a,app} = (E_{a,4+} + \Delta H_2 + \Delta H_3) + \theta_* \Delta H_1 - (\theta_{H,s} + \theta_{KH,*}) \frac{\Delta H_2}{2} - \theta_{KH,*} \Delta H_3 \quad (27)$$

In low temperature coverage regimes, where ‘*’ sites are alkoxy-dominated ($\theta_{KH,*} \approx 1.0$, $\theta_* \approx 0.0$) and ‘s’ sites are mostly vacant ($\theta_{H,s} \approx 0$, $\theta_s \approx 1$), the apparent barrier reduces to $\approx E_{A,4+} + 0.5\Delta H_2$, where $E_{A,4}$ is the elementary barrier of step 4 (≈ 66 kJ mol⁻¹) and ΔH_2 is the enthalpy of dissociative hydrogen chemisorption (≈ -30 kJ mol⁻¹). Thus, the difference between elementary and apparent barriers on alkoxy dominated/hydrogen sparse surfaces (predicted at low

temperatures) is primarily given by the enthalpy of dissociative hydrogen chemisorption, which is independent of the chain length of the ketone. Accordingly, apparent barriers are identical for C₃ – C₅ ketones at low reaction temperatures ($\approx 50 \text{ kJ mol}^{-1}$) despite each species having unique adsorption (ΔH_1) and reaction enthalpies (ΔH_3).

At elevated temperatures, alkoxy and hydrogen coverages decrease and vacant sites become increasingly significant in ‘*’ and ‘s’ site balances. In these coverage regimes, ΔH_1 ($\approx -80 \text{ kJ mol}^{-1}$), ΔH_2 ($\approx -30 \text{ kJ mol}^{-1}$), and ΔH_3 ($\approx -17.5 \text{ kJ mol}^{-1}$) all influence the apparent barrier. Since each step is exothermic, this necessarily leads to a decrease in the apparent barrier relative to the elementary barrier of the rate controlling step. Furthermore, the effects of reaction enthalpies become increasingly pronounced as θ_* and θ_s both approach 1. In this limit, the apparent barrier is reduced by the full magnitude of ketone and hydrogen adsorption enthalpies. This most likely explains our observation of a significantly diminished apparent barrier for acetone hydrogenation ($\approx 18 \text{ kJ mol}^{-1}$) at 442 K.

5. Conclusion

We have considered the hydrogenation of C₃-C₅ ketones over Ru/SiO₂, probing reaction kinetics over a range of ketone partial pressures (0.3 – 30 Torr), H₂ partial pressures (90 – 900 Torr), and reaction temperatures (303 and 456 K). Independent of the ketone, hydrogenations exhibit identical trends in apparent kinetics at low temperatures. Hydrogenation of acetone, 2-butanone, and 2-pentanone occur with an apparent barrier of approximately 50 kJ mol^{-1} between 303 and 363 K. In this temperature range, we additionally observe zero and half order dependencies on the ketone and molecular hydrogen. This suggests that all hydrogenations are described by a similar set of elementary reactions and rate controlling processes. Apparent kinetics are sensitive

to the reaction temperature, with reaction orders during acetone hydrogenation increasing for both the ketone and hydrogen as a function of reaction temperature. This is attributed to reduced coverages of hydrogen and adsorbed hydrocarbons at elevated temperatures, a second consequence of which is that the apparent barrier also decreases with reaction temperature. As surfaces become dominated by vacant sites, exothermic heats of adsorption increasingly influence the observed kinetic barrier, decreasing it to below 20 kJ mol^{-1} at temperatures above roughly 420 K. Measured site time yields and apparent kinetic parameters were reconciled with elementary phenomena by developing a microkinetic model based on a Horiuti-Polanyi scheme in which hydrogen adatoms sequentially saturate surface-adsorbed ketones to form the alcohol. To explain our observation that zero-order kinetics persist over several orders of magnitude in ketone partial pressure, we invoke the assumption that hydrogen atoms and hydrocarbons adsorb at distinct surface sites, which is justifiable based on spectroscopic analysis of adsorbates on Ru(0001) surfaces. Kinetic data are well-described by assuming that the addition of a hydrogen atom to the surface bound alkoxy controls the overall rate of hydrogenation. Parameter estimation suggests that the kinetics of the rate controlling step are, at an elementary level, roughly independent of chain length, proceeding with a kinetic barrier of 66 kJ mol^{-1} and a pre-exponential factor of $\approx 10^{11} \text{ s}^{-1}$. Experimentally, we do observe that measured STYs decrease with ketone chain length. In our model, this is captured by activation entropies becoming increasingly unfavorable with chain length, which is a possible explanation for the observed trend. Alternatively, the observed trend may reflect a failure to properly account for differences in the number of adsorption sites required for acetone, 2-butanone, and 2-pentanone binding. It stands to reason that ketone monolayer coverages will decrease with chain length. This would

likely manifest as a decrease in observed site time yields, for which site counts were estimated by CO uptake, with the size of the ketone.

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Elementary step

Surface Reaction

1. $K + * \xrightleftharpoons{K_1} K_*$
2. $H_2 + 2s \xrightleftharpoons{K_2} 2H_s$
3. $K_* + H_s \xrightleftharpoons{K_3} KH_* + s$
4. $KH_* + H_s \xrightarrow{k_{4+}} A_* + s$
5. $A + * \xrightleftharpoons{K_5} A_*$