Journal of Catalysis 314 (2014) 149-158

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Reaction kinetics and mechanism of ketonization of aliphatic carboxylic acids with different carbon chain lengths over Ru/TiO₂ catalyst

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ARTICLE INFO

Article history: Received 4 February 2014 Revised 5 April 2014 Accepted 9 April 2014

Keywords: Carboxylic acid Ketonization TiO₂ Kinetics β-Ketoacid Transition state

ABSTRACT

A kinetics study of the ketonization of carboxylic acids with varying alkyl chain lengths (acetic, propionic, and butyric) has been conducted on a pre-reduced Ru/TiO_2 catalyst. A thorough analysis built upon a Langmuir–Hinshelwood (LH) model and transition state theory (TST) shows that the reaction follows a second-order expression with respect to the surface coverage of carboxylic acids. The heats of adsorption are very similar for the three different acids and independent of the carbon chain length. Moreover, they are significantly higher than those of the reaction products, that is, ketone, water, and CO_2 . At the same time, the change in adsorption entropy of the acids (in absolute value) with respect to the gas phase was found to decrease with increasing alkyl chain length. These results are consistent with a strongly adsorbed bidentate configuration, in which the main interaction of the LH model in the fitting of the reaction data at varying temperatures allowed us to calculate the true activation energy and the activation entropy of the reaction. Both were found to increase with increasing carbon chain length of the acids. This compensation effect can be interpreted in terms of the nature of the transition state, in which the formation of the C–C bond is the rate-limiting step.

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1. Introduction

Ketonization of carboxylic acids is a well-known reaction, discovered in 1858 by Friedel [1], and widely used in the early 20th century for commercial production of acetone [2]. In recent years, ketonization has received renewed attention for its potential application in the production and upgrading of renewable fuels and chemicals from conversion of cellulosic biomass [3–6]. Fast pyrolysis, that is, rapid heating of biomass in inert environment, produces bio-oil, a complex liquid that is rich in oxygenated molecules. Among them, small acids such as acetic acid are particularly abundant [7]. Therefore, an effective method to deal with these undesirable acids is ketonization, which not only reduces acidity and O content, but also creates C–C bonds that allow keeping the short molecular fragment in the liquid fraction.

For more than thirty years, extensive research efforts have been devoted to the study of surface-catalyzed ketonization. It is generally accepted that reducible amphoteric metal oxides, such as TiO₂, CeO₂, ZrO₂, and MnO₂, are the most effective catalysts for this reaction [8,10]. While some aspects of the mechanism are well

established, others remain unsettled. For example, there is compelling evidence in favor of the crucial role of α -hydrogen on at least one of the two participating carboxylic acid molecules [3,9–11]. However, the exact nature of the reaction intermediates is controversial, and several possibilities have been considered. For example, important roles of acid anhydrides, β -ketoacids, ketene, and ketene-like species have been proposed in different studies [9–14].

Recently, we have investigated the ketonization of acetic acid on well-characterized Ru/TiO₂ catalysts [15,16]. The apparent reaction orders obtained from a simplified power law fitting suggested that the most likely mechanism involves the pseudo-equilibrated competitive adsorption of reactants and products and a bimolecular rate-limiting step that forms the crucial β -ketoacid intermediate.

Rigorous catalytic kinetics analysis is a powerful tool for determining kinetic and thermodynamic parameters that can shed light on the reaction mechanisms and has been successfully applied to many reactions [17,18]. In the present contribution, we attempt to gain a deeper understanding of the ketonization reaction mechanism and reaction intermediates through a detailed kinetic investigation, using a Langmuir–Hinshelwood model, combined with the transition state theory analysis. This combination has allowed us to determine the kinetically-relevant step, and its true







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activation energy instead of the apparent activation energies typically calculated when a detailed kinetic model is not used. More importantly, the data analysis based on the transition state theory provides useful information about the nature of the activated complex.

2. Experimental

2.1. Catalyst synthesis

The 5 wt% Ru/TiO₂ catalyst used in this study was prepared by incipient wetness impregnation of an aqueous solution of RuCl₃. nH_2O (Sigma-Aldrich, 99.5%) onto TiO₂ support (Degussa P25), using a liquid/solid ratio of 0.25 ml/g. After impregnation, the catalyst was dried overnight at 90 °C in a vacuum oven. The dry catalyst was then heated for 3 h at 400 °C under 100 ml/min flow of high-purity air and stored.

2.2. Catalyst characterization

The catalyst was characterized following the procedure described in previous studies [15,16], and the results are summarized in Supporting information. Briefly, the BET surface area of the catalyst was measured by N₂ physisorption at liquid nitrogen temperature on a Micromeritics ASAP 2010 unit. For these measurements, the sample was degassed for 3 h at 250 °C prior to analysis. X-ray diffraction (XRD) analysis was conducted on a Rigaku automatic diffractometer (Model D-MAX A), equipped with a curved crystal monochromator at a system setting of 40 kV and 35 mA. Data were collected over 5-40° angle range with a step size of 0.05° and a count time of 1.0 s. X-ray photoelectron spectroscopy (XPS) data were recorded on a Physical Electronics PHI 5800 ESCA system with standard non-monochromatic Al X-rays (1486.6 eV) operated at 250 W and 15 kV in a chamber pumped down to a pressure of approximately 1.0×10^{-8} Torr. A 93.9 eV and 58.7 eV pass energy were typically used for survey and specific element analysis, respectively.

2.3. Kinetic measurements

The vapor-phase conversion of three carboxylic acids of varying alkyl chain lengths (acetic, propionic, and butyric acids) was measured over Ru/TiO₂ in an isothermal tubular reactor equipped with high-precision flow and temperature controllers. In each run, a fresh catalyst sample was held at the center of a vertical tubular quartz reactor (6 mm I.D.) between two layers of quartz wool. Before the reaction, the catalyst was reduced in situ for 1 h at 400 °C under a 50 ml/min flow of H₂. After reduction, the reactor was cooled down to the selected reaction temperature (275-335 °C) under He flow. The acid feed was continuously injected from a syringe pump and vaporized into the He carrier gas stream to reach the selected space times (W/F) and partial pressures. The outlet of the reactor was connected to a six-way gas sampling valve and heated at 180-200 °C to avoid condensation. The reactants and products were analyzed online by gas chromatography using flame ionization detector (FID) and thermal conductivity detector (TCD). The GC-FID analyses were performed using a Hewlett Packard 6890 GC equipped with a Phenomenex ZB-Wax polyethylene glycol column (30 m \times 0.25 mm \times 0.25 μ m). The GC-TCD analyses were conducted on a Carle 400 AGC with a built-in MultiCoat[™] column. In each run, the carbon balance was checked and found to be higher than 90% in all cases. In order to compare the runs under identical conditions, a fresh catalyst was used in each separate experiment. Following established criteria [19,20], calculations were performed to ensure that external and internal

mass transfer limitations were eliminated (see Supporting information).

3. Results

3.1. Ketonization products from the various acids

One of the advantages of the ketonization reaction is its very high selectivity to the desired products, which greatly simplifies the analysis. Water, CO_2 , and corresponding ketones are practically the only products obtained, in line with the following reaction equation:

$RCOOH + RCOOH \rightarrow RCOR + CO_2 + H_2O$

With acetic and propionic acids, these products were the only ones detected. With butyric acid, they represented >99% of the products, and only trace amounts of larger condensation products were obtained.

3.2. Kinetics results

Our previous study [16] suggested that the ketonization reaction is second order with respect to the surface concentration of adsorbed acid and all the reaction products competing for the same sites, thus inhibiting the reaction rate. From these preliminary results, a series of elementary steps can be proposed and incorporated in a conventional Langmuir–Hinshelwood kinetic model to describe the reaction kinetics.

$$\mathsf{RCOOH} + \ast \xleftarrow{^{K_{\mathsf{Acid}}}} \mathsf{RCOOH} \ast \tag{1}$$

$$\operatorname{RCOR} + \ast \xleftarrow{K_{\operatorname{Ketone}}} \operatorname{RCOR} \ast$$
(2)

$$CO_2 + \ast \xleftarrow{K_{CO_2}} CO_2 \ast$$
(3)

$$H_2O + \ast \xleftarrow{K_{H_2O}} H_2O \ast \tag{4}$$

$$\operatorname{RCOOH} * + \operatorname{RCOOH} * \xrightarrow{k} \operatorname{RCOR} * + \operatorname{CO}_2 + \operatorname{H}_2\operatorname{O} + *$$
(5)

where * represents a surface active site.

It is important to mention that for the rate-determining step (5), the critical kinetic parameter is the rate constant, which provides information about the activation barrier. This barrier is the energy difference between the stable adsorbed species, RCOOH and the transition state. While the formation of the stable products may still require several subsequent steps, the formation (or decomposition) of the transition state is the crucial, rate-limiting step. Therefore, there are two possible transition states that can be considered in this step, as illustrated in Fig. 1. In the first case, the transition state would be one in which the C-C bond is still rather long, while the C-COO bond that connects the CO₂ to the molecule is still rather short. We consider this as an *early* transition state. By contrast, in the second case, the C-C bond to be formed is shorter and the C-COO bond that will break upon reaction is now rather long. We therefore consider this as a late transition state.

$$\begin{split} \text{RCOOH} * + \text{RCOOH} * &\rightarrow [\text{RCO} \cdots \text{RCOO}^{\#}] * + \text{H}_2\text{O} + * \\ &\rightarrow \text{RCOR} * + \text{CO}_2 + \text{H}_2\text{O} + * \end{split} \tag{5a}$$

$$\begin{split} \text{RCOOH} * + \text{RCOOH} * &\rightarrow [\text{RCOR} \cdots \text{COO}^{\#}] * + \text{H}_2\text{O} + * \\ &\rightarrow \text{RCOR} * + \text{CO}_2 + \text{H}_2\text{O} + * \end{split} \tag{5b}$$



Reaction coordinate

Fig. 1. Proposed early and late transition state (TS) structures for ketonization of carboxylic acids.

Accordingly, the measured activation energy will be either the energy required to bring the two C atoms together and form the C–C bond between the two adsorbed acid species (*early* transition state) or the energy needed for decarboxylation (i.e., CO_2 detachment) of the β -ketoacid intermediate (*late* transition state). As will be discussed below, the two proposed transition states might be subject to steric effects that may vary to different extents with different alkyl chain lengths.

Based on the elementary steps proposed above with step (5) as the rate-limiting step, the overall reaction rate can be expressed as follows:

$$rate = k(\Theta_{\rm RCOOH})^2 \tag{6}$$

where Θ_{RCOOH} is the fractional coverage of the carboxylic acid and can be derived from the adsorption equilibrium and the pseudo-equilibrated steps by the conventional expressions:

$$\Theta_{\rm RCOOH} = K_{\rm RCOOH} P_{\rm RCOOH} \Theta_{\rm V} \tag{7}$$

 $\Theta_{\rm RCOR} = K_{\rm RCOR} P_{\rm RCOR} \Theta_{\rm V} \tag{8}$

$$\Theta_{\rm CO_2} = K_{\rm CO_2} P_{\rm CO_2} \Theta_{\rm V} \tag{9}$$

$$\Theta_{\rm H_2O} = K_{\rm H_2O} P_{\rm H_2O} \Theta_{\rm V} \tag{10}$$

where Θ_V is the fraction of empty sites, while Θ_{RCOR} , $\Theta_{\text{H}_2\text{O}}$, and Θ_{CO_2} are the fractional surface coverages of ketone, water, and CO₂, respectively.

Applying the conventional Langmuir–Hinshelwood kinetics derivation, the rate expression becomes:

$$rate = k \frac{(K_{\rm RCOOH} P_{\rm RCOOH})^2}{(1 + K_{\rm RCOOH} P_{\rm RCOOH} + K_{\rm RCOR} P_{\rm RCOR} + K_{\rm CO_2} P_{\rm CO_2} + K_{\rm H_2O} P_{\rm H_2O})^2}$$
(11)

To better validate the kinetic model and fitting parameters obtained, two sets of data were used for the analysis of the ketonization of acetic acid at 275 °C. The first set of data obtained with the same (initial) acetic acid feed composition was analyzed by the integral reactor method at different space times (W/F). The second set of data was analyzed by the differential reactor method, in which the composition of the feed is varied with different concentrations of acetic acid and products, working at short W/F and consequently low conversions. Both sets of data were successfully fitted with the same values of kinetic fitting parameters, which reflect the robustness of the fitting.

Fig. 2 shows a parity plot of the experimental rates of acetic acid ketonization obtained with different feed compositions to the calculated rates by using Eq. (11) in the differential reactor method.

The fitting parameters were obtained simultaneously with the data set obtained from the runs using the same initial feed composition at different space times (W/F) in the integral reactor, which is illustrated in Fig. 3a.

Fig. 3a–c shows the evolution of partial pressures of reactant and product as a function of W/F for three different temperatures (275, 280, and 285 °C) in an isothermal integral reactor. The corresponding results obtained for propionic acid (290, 300, and 310 °C) and butyric acid (315, 325, and 335 °C) are shown in Figs. 4 and 5, respectively. The solid lines in each case represent the fitted partial pressures using the same Langmuir–Hinshelwood model described above. The thermodynamic and kinetic constants are expressed as a function of temperature according to the conventional Arrhenius and Van't Hoff equations in terms of the true activation energy (*E*) and enthalpies (ΔH) and entropies (ΔS) of adsorption, respectively. That is, $k_i = Ae^{\frac{K}{RT}}$ and $K_i = e^{\frac{K}{RT}}e^{\frac{-MH_i}{RT}}$. It must be noted that the adsorption enthalpy and entropy values for water and CO₂ were kept the same in the fitting of the three acids at all temperatures.

The equilibrium adsorption constants for the three acids, three ketones, water, and CO_2 resulting from the fitting at different temperatures are summarized in Tables 1–3. Remarkably, the resulting enthalpies of adsorption for the three acids are significantly higher than those of the reaction products, which decrease in the order of ketones > CO_2 > water.

It is important to note that as shown in Fig. 6, all three acids have very similar heats of adsorption (i.e., about 134 kJ/mol), but the entropies of adsorption exhibit a significant change with increasing alkyl chain length from acetic acid to butyric acid (i.e., from –198 to –178 J/mol K). Vannice [20,21] has recommended a set of criteria to further validate the thermodynamic parameters extracted from kinetic fittings. The ΔS_{ads} must be negative, and its absolute value must be smaller than the standard entropy in the vapor phase. Indeed, both criteria have been met for the calculated ΔS_{ads} values of all species involved in the kinetics analysis.

In contrast to the acids, the absolute values of the changes in both adsorption enthalpy and entropy of the ketones increase with the alkyl chain length with respect to the gas phase (see Fig. 6b). In comparison with the adsorption constants of the acids (K_{Acid}), the constants of the ketones (K_{Ketone}) are smaller, but still significantly higher than those of water and CO₂, which indicates that these two



Fig. 2. Parity plot comparison of experimental data (the points) obtained with differential reactor model with the fitted data from Langmuir–Hinshelwood model (the line).



Fig. 3. Partial pressures of acetic acid and acetone as a function of W/F at 30-min time on stream on Ru/TiO₂ catalyst at 275, 280, and 285 °C. Catalysts were prereduced in H₂ stream at 400 °C in 1 h. The points are experimental data, and the lines are fitted data from the Langmuir–Hinshelwood fitting model.

products would only compete weakly for adsorption sites during the reaction. In fact, as shown in Fig. 7, when the fractional surface coverages of acid, ketone, water, and CO_2 are calculated as a function of conversion, we can see that at low conversion, the surface is practically covered by the carboxylic acid, and only at the highest conversion levels is the ketone a strong adsorption competitor. In all cases, the coverages of water and CO_2 were kept very low for the entire conversion range. Therefore, during the course of the reaction, ketones are the strongest inhibitors of ketonization activity, which is consistent with our previous report [16].

Tables 1–3 also include the kinetic rate constants (k_i) obtained from the fittings for the three different acids. Since this rate



Fig. 4. Partial pressures of propionic acid and 3-pentanone as a function of W/F at 30-min time on stream on Ru/TiO_2 catalyst at 290, 300, and 310 °C. Catalysts were pre-reduced in H₂ stream at 400 °C in 1 h. The points are experimental data, and the lines are fitted data from the Langmuir–Hinshelwood fitting model.

constant corresponds to the individual rate constant of the ratelimiting step in the mechanism, the *E/R* values calculated for each acid from the slopes of the Arrhenius plots (Fig. 8) correspond to the true activation energies. Accordingly, the resulting values are 161, 186, and 225 kJ/mol for the ketonization of acetic, propionic, and butyric acids, respectively. The value of 161 kJ/mol found for acetic acid is in close agreement with activation energy values previously reported. For example, Kuriacose and Rajadurai [22] working below 400 °C obtained a value of 159 kJ/mol for the true activation energy over Zn:Cr:Fe mixed oxides and 141 kJ/mol over iron oxide [23]. By contrast, the value reported for the reaction over ZrO₂ was noticeably higher, 193 kJ/mol [11,24]. As shown in



Fig. 5. Partial pressures of butyric acid and 4-heptanone as a function of W/F at 30min time on stream on Ru/TiO₂ catalyst at 315, 325, and 335 °C. Catalysts were prereduced in H₂ stream at 400 °C in 1 h. The points are experimental data, and the lines are fitted data from the Langmuir–Hinshelwood fitting model.

Fig. 9, a clear trend is observed in the true activation energy as a function of alkyl chain length. As discussed in more detail below, this trend can shed light on the nature of the transition state for the ketonization reaction.

4. Discussion

4.1. Nature of catalyst active sites

Our earlier work has demonstrated that Ru alone is inactive for ketonization. In fact, when Ru is supported on an inert support such as carbon, no ketonization activity was detected under conditions at which Ru/TiO₂ shows significant conversion [15,16]. However, the addition of Ru significantly enhances the ketonization activity of a reducible oxide, such as TiO₂. A detailed characterization of the catalysts indicated that the catalytically active sites for ketonization are coordinatively unsaturated Ti cations, whose presence can be enhanced by Ru, which greatly facilitates the reducibility of TiO₂, that is, the formation of surface Ti³⁺ species [15,16]. Similar mechanisms have been proposed in the earlier literature [25,26]. The detailed kinetic investigation in this study provides a quantitative evidence to support this conclusion.

For all the temperatures and acid types tested in this study, the adsorption of acids was found to be significantly stronger than that of ketones, water, or CO₂, which favors the ketonization reaction, in agreement with our previous reports [15,16]. Among the three products, ketones are the more strongly adsorbed, and as shown in Fig. 7, they compete more effectively with the acids for active sites than the other products. In previous studies [27], ketones have been shown to preferentially bind to coordinatively unsaturated Ti cation sites through the oxygen atom of the carbonyl group in an η^1 coordination, which correlates well with the proposed nature of the ketonization active sites.

Similarly, the observed negative effect of water on catalyst activity is likely due to its competitive adsorption with acid to the surface cations as coordination sites [28]. Likewise, CO₂ could potentially impede the reaction through either the formation of carbonate or adsorbed CO₂ via Ti-O-C-O bonding on the catalyst surface [29]. However, in comparison with ketones, water and CO₂ have a much lower inhibiting effect on ketonization activity. The weak adsorption of water on TiO₂ is consistent with previous reports by Deng et al. [30]. By contrast, the influence of CO_2 on ketonization activity seems to be highly dependent on the support properties. For example, Gaertner et al. [31] have shown that the ketonization activity of a ZrO₂-CeO₂ catalyst was drastically reduced upon the addition of CO₂ and water. This apparent contradiction with the results reported here is most likely due to the higher basicity of CeO₂ than TiO₂, forming strongly adsorbed carbonate on CeO₂ surface.

4.2. Nature of the adsorbed species under reaction conditions

The strong heats of adsorption derived from the kinetics for the three acids do not depend on the length of the alkyl chain. As shown in Fig. 6, the Langmuir-Hinshelwood kinetic fitting results yield almost identical heats of adsorption for acetic, propionic, and butyric acids on Ru/TiO₂ catalyst. Moreover, experimental studies, such as scanning tunneling microscopy [32] and vibrational spectroscopy [35], as well as computational studies involving ab initio slab calculations [33] have shown that the most stable adsorption mode of monocarboxylic acids, such as formic and acetic acids, on either anatase or rutile TiO₂ is the bridging (bidentate) configuration, in which two oxygen atoms of carboxylates bound to two surface Ti cations. Therefore, one can conclude that under reaction conditions, the acids adsorb via formation of a bidentate species strongly bound to the surface through the two O on the carboxylic group, but with little or no interaction of the alkyl chain with the surface.

Reported direct measurements of heats of adsorption of these acids on TiO_2 include a distribution of values, which are in the same range as those derived from our kinetics study. For example, Bowker et al. [34] have measured heats of dissociative adsorption of formic acid on TiO_2 (110) single crystals on the order of 125 kJ/ mol. For Wang et al. [35], the heat of adsorption of acetic acid on anatase was around 100 kJ/mol, while Idriss et al. [36,37] obtained essentially the same heats of adsorption, about 160 kJ/mol, for formic and acetic acids on TiO_2 (110). While this absolute value is somewhat higher than those found in our work, the constant heat

Table 1

Optimized kinetic and thermodynamic parameter values for the ketonization of acetic acid obtained from fitting the experimental data with the Langmuir–Hinshelwood kinetic model.

| Temp (°C) | Rate constant | nol/g cat h), k Adsorption constant (Torr ⁻¹) | | | | |
|--|---------------|---|--------------------------|----------|--------------------|------------------|
| | | | K _{Acetic acid} | KAcetone | K _{Water} | K _{CO2} |
| 275 | 0.057 | | 0.362 | 0.231 | 0.033 | 0.019 |
| 280 | 0.080 | | 0.274 | 0.194 | 0.029 | 0.016 |
| 285 | 0.108 | | 0.214 | 0.150 | 0.024 | 0.014 |
| | | Acetic | Acetone | Wa | ater | CO ₂ |
| $\Delta H_{\rm adsorption}$ (kJ/mol) | | -133.97 | -109.73 | _ | 81.80 | -87.54 |
| $\Delta S_{\text{adsorption}}$ (J/mol K) | | -197.74 | -157.10 | -1 | 22.36 | -137.43 |
| Sgas (J/mol K) (upper bound) | | 282.8 | 293.1 | 1 | 88.8 | 213.8 |

Table 2

Optimized kinetic and thermodynamic parameter values for the ketonization of propionic acid obtained from fitting the experimental data with the Langmuir-Hinshelwood kinetic model.

| Temp (°C) | Rate constant | t (mol/g cat h), <i>k</i> | Adsorption constant (Torr ⁻¹) | | | |
|--------------------------------------|---------------|---------------------------|---|------------------------|--------------------|------------------|
| | | | K _{Propionic acid} | K _{Pentanone} | K _{Water} | K _{CO2} |
| 290 | 0.023 | | 0.396 | 0.273 | 0.021 | 0.011 |
| 300 | 0.050 | | 0.230 | 0.174 | 0.015 | 0.008 |
| 310 | 0.088 | | 0.148 | 0.115 | 0.011 | 0.006 |
| | | Propionic | 3-Pentanone | Wa | ter | CO_2 |
| $\Delta H_{\rm adsorption}$ (kJ/mol) | | -134.15 | -117.80 | -1 | 31.80 | -87.54 |
| $\Delta S_{adsorption}$ (J/mol K) | | -190.17 | -169.73 | -12 | 22.36 | -137.43 |
| S _{gas} (J/mol K) (upper bo | ound) | - | - | 18 | 38.8 | 213.8 |

Table 3

Optimized kinetic and thermodynamic parameter values for the ketonization of butyric acid obtained from fitting the experimental data with the Langmuir–Hinshelwood kinetic model.

| Temp (°C) | Rate constant | (mol/g cat h), k | Adsorption constant (Torr ⁻¹) | | | |
|--------------------------------------|---------------|------------------|---|------------------------|--------------------|------------------|
| | | | K _{Butyric acid} | K _{Heptanone} | K _{water} | K _{CO2} |
| 315 | 0.012 | | 0.584 | 0.275 | 0.010 | 0.005 |
| 325 | 0.024 | | 0.304 | 0.179 | 0.007 | 0.004 |
| 335 | 0.055 | | 0.102 | 0.051 | 0.003 | 0.002 |
| | | Butyric | 4-Heptanone | Wa | ter | CO ₂ |
| $\Delta H_{\rm adsorption}$ (kJ/mol) | | -134.63 | -129.51 | _ | 81.80 | -87.54 |
| $\Delta S_{adsorption}$ (J/mol K) | | -178.43 | -175.73 | -1 | 22.36 | -137.43 |
| Sgas (J/mol K) (upper bound | 1) | 353.3 | - | 1 | 88.8 | 213.8 |

of adsorption for different acids is in good agreement with our observations.

It is essential to point out that while the adsorption enthalpies were basically constant for the three acids, the adsorption entropies changed considerably and systematically. It was found that, relative to their gas phase values, acetic acid showed the highest loss of entropy upon adsorption, while butyric acid showed the lowest. That is, compared to the gas phase, the loss in entropy upon adsorption appears to decrease with increasing length of the alkyl group. This trend can be rationalized in terms of the proposed adsorption species. That is, the number of degrees of freedom that can be retained in the molecule upon anchoring the end carboxylic group to the surface, while leaving the alkyl chain free, directly increases with the alkyl chain length. Therefore, together with the observed constant adsorption enthalpy values, the observed trend in entropy gives further support to the picture of a bidentate carboxylate adsorbed species, with the alkyl group not interacting with the surface or interacting only weakly.

4.3. Nature of the transition state

The transition state theory can provide a physical justification to the kinetic parameters derived from the fitting as well as some insight into the structure and configuration of the transition state involved in the chemical reaction. The transition state theory assumes the occurrence of an activated complex that is in equilibrium with reactants and readily converts into products in a single vibration.

As proposed above, the rate-limiting step (5) can be described by the following equations:

$$RCOOH * + RCOOH * \xleftarrow{K^{\#}} [2RCOOH^{\#}] * \xleftarrow{\nu^{\#}} RCOR * + CO_2 + H_2O + *$$
(13)

where [2RCOOH[#]] can be either [RCO···RCOO[#]] or [RCOR···COO[#]] for early and late transition states, respectively

From this equation, the ketonization rate, as derived from transition state theory, will be equal to the concentration of the



Fig. 6. Adsorption enthalpies and entropies as function of carbon chain length of acid (a) and ketones (b) over Ru/TiO_2 catalyst.

activated complex multiplied by the frequency at which the new C–C bond is formed.

$$rate = v^{\#} K^{\#} ([2RCOOH^{\#}]_{*})^{2}$$
(14)

where $v^{\#}$, the vibration along the reaction coordinate, corresponds to the vibration of the C–C bond being formed. The equilibrium constant $K^{\#}$, based on statistical mechanics, can be written as follows:

$$K^{\#} = q_{\rm vib}^{\rm asym} K^{\prime \#} \tag{15}$$

in which $q_{\rm vb}^{\rm asym}$ is the partition function for the loose antisymmetric vibrational mode along the reaction coordinates, leading to the formation of the new C–C bond, and $K'^{\#}$ represents the equilibrium constant with the loose vibration removed. The loose vibration is fully excited (high-temperature limit) and can be described by the expression:

$$q_{\rm vib}^{\rm asym} = \frac{1}{1 - e^{-h\nu^{\#}/k_BT}} \approx \frac{k_B T}{h\nu^{\#}}$$
(16)

Canceling $v^{\#}$ in (15) with the derived partition function for the C–C bond vibration stretch at the transition state (17) gives the following:

rate =
$$v^{\#} \frac{k_B T}{h v^{\#}} K'^{\#} ([2RCOOH^{\#}]*)^2 = \frac{k_B T}{h} K'^{\#} ([2RCOOH^{\#}]*)^2$$
(17)

where k_B and h are the Boltzmann and Planck constants, respectively, and $K'^{\#}$ is the transition state equilibrium constant (calculated from partition functions for the activated complex which



Fig. 7. Surface fraction coverage of acid, ketone, water, and CO_2 as a function of conversion over Ru/TiO_2 catalyst.



Fig. 8. Arrhenius plot of ketonization rate constants for the three carboxylic acids.



Fig. 9. Ketonization activation energies as a function of carbon chain length. Error bars indicate 95% confidence interval.

exclude the C–C bond stretch along the reaction coordinate). This $K^{\#}$ value reflects the enthalpy and entropy of activation, which can be readily calculated from data at varying temperatures using the Eyring–Polanyi expression:

$$rate = \frac{k_B T}{h} e^{-\Delta H^{\#}/RT} e^{\Delta S^{\#}/R} ([2RCOOH^{\#}]*)^2$$
(18)

It is important to note that the rate in transition state analysis is on a per catalytic active site basis, which is calculated as follows:

Number of catalyst sites = Catalyst mass (g)

$$\begin{array}{l} \times \text{ Catalyst surface area } (m^2/g) \\ \times \text{ Ti cation density } (\text{Ti sites}/nm^2) \\ \times 10^{18} \ nm^2/m^2 \end{array}$$

To obtain the catalyst surface area in this expression, BET measurements were conducted on the catalyst. The density of Ti cations was obtained from prior surface science studies [38].

In some kinetics studies, the barriers derived from fitting pseudo first-order rate expressions are "apparent" values, relative to the gas phase [18,39]. It is important to note that since we use a full LH equation to fit the reaction rate measurements, the rate constant thus derived includes the true enthalpy and entropy of activation for the C–C bond formation (or breaking) with respect to the surface adsorbed species (single elementary step (5)). Therefore, the values of $\Delta H^{\#}$ and $\Delta S^{\#}$ in Eq. (18) refer to the differences between the *H* and *S* values of the transition state and those of the adsorbed reactants (i.e., two adsorbed acid molecules).

The goodness of the kinetic fitting for a second-order LH model with respect to adsorbed acid coverage is consistent with the proposed mechanism that involves two adsorbed carboxylate species on the surface that form a β -ketoacid intermediate, as previously discussed [3,10,24].

Table 4 summarizes the resulting activation enthalpies and entropies of acetic, propionic, and butyric acid, respectively. It is clear that the activation enthalpy ($\Delta H^{\#}$) increases monotonically with increasing alkyl chain length, which can be described as an increased energy barrier for the rate-limiting step as the size of the alkyl chain increases. Similarly, the changes in activation entropies $\Delta S^{\#}$ are positive and also increase as a function of carbon chain length. That is, the entropy of the transition state is higher

Table 4

Activation enthalpies and entropies for ketonization of acetic, propionic, and butyric acid over Ru/TiO_2 catalyst.

| | Activation enthalpy, ΔH (kJ/mol) | Activation entropy, ΔS (J/mol K) |
|----------------|---|---|
| Acetic acid | 156.4 | 3.4 |
| Propionic acid | 181.5 | 32.4 |
| Butyric acid | 220.0 | 78.2 |

than that of the two adsorbed acids and more interestingly, the entropy gain increases with the length of the alkyl chain. That is, there seems to be a correlation between entropy and enthalpy.

In fact, as shown in Fig. 10a, the well-known compensation effect [40–42] is clearly apparent in these data. Bond et al. [43,44] have suggested that the compensation effect may be a result of using apparent activation enthalpy and entropy. However, we must emphasize that in this work, the compensation effect is observed with true enthalpy and entropy (see Fig. 10b).

Many years ago, Everett [45] made the observation of the commonly observed linear relationship between entropy and enthalpy of adsorption, which can be interpreted taking into account that a greater binding energy of the molecule to the surface would restrict its vibrational and rotational degrees of freedom. This is not the case in our system, in which no compensation effect is observed for the adsorption. In fact, the heats of adsorption remained constant as a function of the alkyl chain length, but the entropy of adsorption did increase due to a greater number of degrees of freedom with increasing chain length. By contrast, the compensation effect was in fact observed for the enthalpies and entropies of activation, when the transition state was involved, which gives us more information about the nature of this species and, consequently, sheds light on the reaction mechanism.

As mentioned above, the ketonization can either go through an early or a late transition state, depending on the position of the energy peak along the reaction coordinate. The early transition state involves the formation of the C–C bond between the two adsorbed carboxylates, leading to the formation of the β -ketoacid (RCO \cdots RCOO) intermediate, as proposed in our earlier study [16]. In contrast, the late transition state involves the decarboxylation of β -ketoacid (RCOR \cdots COO), as suggested by Renz et al. [46].

The observed trend in activation enthalpy is an increase in the following order, acetic < propionic < butyric. We believe that this trend supports the idea of an early transition state, since we can expect that increasing the alkyl chain length would enhance the energy requirement to overcome the increasing steric repulsion of bulkier alkyl groups that make the formation of the C–C bond more difficult. In other words, larger molecules imply larger spatial hindrance to overcome to reach the appropriate coupling configuration, and therefore a higher energy requirement. In contrast, in the case of the late transition state, one would not expect a higher enthalpy barrier with increasing alkyl chain length. The decarboxylation of β -ketoacid only involves the redistribution of electrons within the ketone and acid functional group [47], which is not only a relatively simple process from an energy requirement point of view, but also independent of the alkyl chain length.

The positive activation entropy for all three acids with respect to the adsorbed state indicates that the bidentate carboxylates go through a transition state with an entropy gain. This is indicative of a structure for the activated complexes with more degrees of freedom than the sum of the two adsorbates.

During the catalytic cycle, the transition state could undergo a transformation to a less restricted adsorption configuration such as monodentate linkage to the surface, but the increase in entropy is most probably related to intramolecular configura-



Fig. 10. Compensation plots for ketonization of acetic, propionic, and butyric acids over Ru/TiO₂ catalysts. Error bars indicate 95% confidence interval.

tional contributions to the entropy. Configurational entropy is the portion of a system's entropy related to the position of its constituent particles or physically related to the number of ways of arranging all the particles of the system. Its partition function becomes larger upon intermolecular coupling in comparison with changes that might occur in the translational, vibrational, and rotational contributions. As a results, the longer the alkyl chain the greater would be the enhancement in configurational entropy, which would explain the observed trend, that is, acetic < propionic < butyric. While one expects the same trend in entropy increase for both early and late transition state cases, the activation entropy trend supports the notion that the ratelimiting step is the formation of a surface dimer with more possible configurations than the adsorbates. Correspondingly, the activation enthalpy trend indicates an early transition state (i.e., formation of the C-C bond).

5. Conclusion

In this study, we have conducted a comprehensive kinetics analysis of the ketonization of carboxylic acids with different alkyl chain lengths over a pre-reduced Ru/TiO₂ catalyst. A Langmuir– Hinshelwood model that considers second-order kinetics with respect to surface coverage of carboxylic acids and competitive adsorption of products can accurately describe the ketonization reaction over a wide range of reaction conditions (temperature, composition) for three different acids. Detailed analysis of the kinetics data revealed significant insights into the reaction.

- (a) The carboxylic acids adsorb on the catalyst surface in a bidentate-bridging mode via the carboxylic group with little or no interaction of the alkyl groups with the surface, as evidenced by the independence of the adsorption enthalpies of acids on carbon chain length and the decreased entropy change upon adsorption of increasingly longer chains.
- (b) Both the enthalpy and entropy of activation for the ketonization reaction increase with increasing alkyl chain length of the acid. Transition state theory analysis suggests that the reaction path proceeds through an early transition state toward the formation of the β-ketoacid intermediate via bimolecular coupling of two surface carboxylates in which the formation of C–C bonds is hindered when the alkyl groups are bulkier.

Acknowledgments

This work was supported by the Department of Energy under Grants DE SC0004600 (catalyst preparation and characterization) and EE0006287 (kinetics measurements). We also would like to thank Drs. S.P. Crossley, T. Sooknoi, and R.E. Jentoft for valuable discussions and technical assistance.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.04.008.

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