**Aldol Condensation of Acetaldehyde and Guerbet Coupling of Ethanol Catalyzed by Hydroxyapatite and Magnesia**

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**Introduction**

The Guerbet coupling of ethanol to butanol has gained interest because of large quantities of ethanol being produced in the United States for use as a fuel additive. Butanol is a more effective fuel additive due to its higher energy density and poor miscibility with water, so finding a method to convert the bio-renewable ethanol to butanol is desirable. Guerbet coupling of ethanol proceeds through a sequence of reactions thought to consist of the dehydrogenation of ethanol to acetaldehyde (AcH), the aldol condensation of AcH to crotonaldehyde (but-2-enal), and the subsequent hydrogenation of crotonaldehyde to 1-butanol. It is currently unclear what steps in this reaction are kinetically relevant, but aldol condensation appears to play a key role [1]. Additionally, aldol condensation is used industrially to produce products like 2-ethylhexanal, isophorone, and mesityl oxide [2].

Both aldol condensation and Guerbet coupling are very sensitive to the acid-base properties of the catalyst used. This study compares two materials to elucidate the effect of acid-base properties on activity and selectivity. Magnesium oxide (MgO), a solid base, and hydroxyapatite (HAP, Ca_{10}(PO_{4})_{6}(OH)_{2}), a bifunctional material, were used to study the aldol condensation of AcH to crotonaldehyde. The rate of crotonaldehyde formation was measured at various AcH partial pressures and multiple temperatures to calculate the intrinsic activation energies (E_a) and heats of adsorption (ΔH_ads) of the catalysts. These parameters along with reactivity data are used to provide insight to the mechanism of Guerbet coupling.

**Materials and Methods**

Vapor phase aldol condensation of AcH to crotonaldehyde and coupling of ethanol to 1-butanol were carried out in a downward-flow fixed bed reactor packed with MgO (Ube Industries) or HAP (synthesized). The product stream was analyzed by gas chromatography using an Agilent DB-WAX 30 m, 530 μm ID column with a flame ionization detector.

**Results and Discussion**

Condensation of AcH occurred over both HAP and MgO with 100% selectivity to crotonaldehyde. The activity of HAP was greater than that of MgO with comparable rates achieved at a temperature 120 K lower. Unfortunately, both catalysts deactivated severely after 8 h on stream. Initial rates were found by fitting results collected over the first 7 h on stream to an empirical hyperbolic function and extrapolating to zero time on stream. A Langmuir-Hinshelwood model was used to fit the initial rates, where enolate formation was assumed to be the rate determining step and AcH was assumed to be the dominant surface species. This model gives the expression in equation 1, where k is the rate constant of enolate formation, K is the equilibrium constant for AcH adsorption, and P_AcH is the partial pressure of AcH.

\[ r = \frac{kP_{AcH}}{1 + KP_{AcH}} \]  

(1)

The values of E_a and ΔH_ads were calculated after the initial rates were collected at multiple temperatures and AcH partial pressures. The reaction on HAP was found to have an E_a of 30 kJ mol\(^{-1}\) and a ΔH_ads of -21 kJ mol\(^{-1}\) while that on MgO had an E_a of 90 kJ mol\(^{-1}\) and a ΔH_ads of -82 kJ mol\(^{-1}\). The low values of ΔH_ads suggest that even initial rates may be measured on partially deactivated surfaces.

As with aldol condensation, Guerbet coupling was observed at much lower temperatures on HAP compared to MgO. The HAP catalyst had a much higher selectivity to butanol, and a much lower selectivity to the side product ethene as shown in Table 1. The decreased selectivity to butanol and increased selectivity to AcH over MgO is likely due to the low rate of aldol condensation at the conditions of Guerbet coupling.

**Significance**

Understanding how acid-base properties of the catalyst affect aldol condensation and Guerbet coupling will allow for the development of more effective catalysts for these reactions.

**Table 1. Rate and Selectivity of Guerbet Coupling of Ethanol**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (K)</th>
<th>Rate (mol s(^{-1}) m(^{-2}))</th>
<th>Ethene (C%)</th>
<th>AcH (C%)</th>
<th>Butanol (C%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAP</td>
<td>613</td>
<td>4.4 x 10(^{3})</td>
<td>1</td>
<td>32</td>
<td>67</td>
</tr>
<tr>
<td>MgO</td>
<td>653</td>
<td>1.4 x 10(^{4})</td>
<td>12</td>
<td>67</td>
<td>13</td>
</tr>
</tbody>
</table>

**Figure 1.** Kinetic model of AcH aldol condensation over HAP (open symbols, dashed line) and MgO (closed symbols, solid line) at different temperatures and a total system pressure of 220 kPa.

**References**
