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Hydrogen Transfer Reactions Relevant to Guerbet Coupling of Alcohols over Hydroxyapatite and Magnesium Oxide Catalysts

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Hydrogenation and dehydrogenation reactions were performed over hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) and magnesia (MgO) to explore their role in the reaction network for the Guerbet coupling of ethanol to butanol. In particular, the dehydrogenation of benzyl alcohol at 633 K and the hydrogenation of ethene and acetone at 473 K using both H_2 and ethanol as a hydrogen source were studied. The H_2-D_2 exchange reaction at room temperature and the Guerbet coupling of ethanol at 613-673 K in the presence of D_2 were also performed. Although there was no consequence of adding D_2 to the Guerbet coupling of ethanol in terms of rate or selectivity, incorporation of deuterium into product butanol was only observed over MgO. This was attributed to the rapid exchange of H_2-D_2 that can occur over MgO but not over HAP. Hydrogenation of acetone occurred with ethanol as a sacrificial hydrogen donor via an MPV-like reaction whereas hydrogenation with H_2 was not observed. Hydrogenation of ethene with H_2 or ethanol was not observed above background. Comparing the rate of benzyl alcohol dehydrogenation to the rate of ethanol coupling over HAP and MgO suggests that the MPV-like hydrogen transfer reaction over HAP is mostly responsible for generating intermediate acetaldehyde during the Guerbet reaction instead of direct dehydrogenation.

1. Introduction

Catalytic reactions involving hydrogen have been well studied for many years. Olefin hydrogenation[1–5], butene isomerization[6,7], and H_2-D_2 exchange[8] are all examples of commonly studied reactions involving hydrogen. The mechanism for H_2 activation is known to be different over metal catalysts compared to basic metal oxides. While H_2 is generally accepted to dissociate into two hydrogen atoms on metal catalysts,[9] H_2 activation either does not occur on basic metal oxides such as MgO, or is heterolytically dissociated to a hydride and a proton[7] over surface acid and base sites, respectively.

Many catalytic reactions involving hydrogen transfer can be important to the rate and desired product selectivity in more complex reaction networks. One example is the Guerbet coupling of alcohols. The Guerbet reaction consists of coupling two short chain alcohols to form a longer chain alcohol and water. The Guerbet coupling reaction has experienced a surge

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in recent interest because it is a potential method to upgrade biorenewable ethanol to butanol as shown in Scheme 1. For more information on the Guerbet coupling reaction see the recent reviews by Kozlowski and Davis[10] and Gabriels et al.[11] Ethanol is a commonly used bio-renewable fuel additive, but it has many drawbacks such as lower energy density and higher corrosivity when compared to gasoline[12]. Guerbet coupling has been studied over many different acid-base catalysts including magnesium oxide[13–15], mixed metal oxides[16,17], hydrotalcites[18], cation exchanged zeolites[19], and metal phosphates[20–24]. Additionally, the Guerbet coupling reaction has been carried out using a heterogeneous metal catalyst coupled with a homogeneous base catalyst[25,26]. Of these, hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) has been shown to be the most active catalyst with high selectivity toward butanol.

A commonly-accepted mechanism for Guerbet coupling, shown in Scheme 2, consists of a sequence of hydrogen transfer and carbon-carbon coupling steps. First, ethanol is dehydrogenated to acetaldehyde, which subsequently, undergoes a self-aldol condensation to form crotonaldehyde (2-butenal). Crotonaldehyde is then hydrogenated to form the saturated product 1-butanol. While this mechanism is supported by many studies[22–24,27], a direct condensation mechanism whereby ethanol self-condenses or condenses with an acetaldehyde molecule has also been proposed[13,15,19,28].

Although many studies have been performed on the overall Guerbet coupling reaction[14,15,19–24,27], the key elementary steps that comprise the reaction path need to be understood to facilitate catalyst design and optimization. In particular, aldol condensation has been studied over catalysts that have demonstrated activity for Guerbet coupling[29–36]. Our previous work on the aldol condensation of acetaldehyde over HAP and MgO showed that surface reactions such as enolate formation are very rapid while the adsorption of acetaldehyde as well as product desorption are kinetically relevant[29]. However, the role of hydrogenation and dehydrogenation reactions during Guerbet coupling over HAP and MgO are much less understood, despite being critical steps in the initial dehydrogenation of ethanol to acetaldehyde as well as the final hydrogenation reactions of crotonaldehyde to butanol. Indeed, the importance of hydrogen transfer reactions during Guerbet coupling has been demonstrated by the promotion of activity by adding metal components to the catalyst[37–39]. The presence of the added metal is thought to increase the rate of Guerbet coupling by facilitating the initial dehydrogenation of ethanol.

In the absence of metal promoters, ethanol dehydrogenation on basic metal oxides typically takes place at relatively high temperatures and is thought to proceed through an E_{1cB} mechanism[40]. Moteki and Flaherty[23] as well as Hanspal et al.[41] have shown that co-feeding H_2 during the Guerbet coupling reaction over HAP has no effect on the rate or selectivity at 548 K and 613 K, respectively. Additionally, Ogo et al.[42] have shown that H_2 is unable to hydrogenate crotonaldehyde to butanol at 573 K. However, when 2-butanol was used as a hydrogen source the formation of 1-butanol from crotonaldehyde via hydrogen transfer was observed.

The observation that H_2 does not change the rate or selectivity of Guerbet coupling over HAP and the ability of an alcohol to hydrogenate crotonaldehyde over HAP suggests that hydrogen transfer occurs through a Meerwein-Ponndorf-Verley-like (MPV-like) mechanism. The MPV reaction consists of the hydrogenation of an aldehyde or ketone through direct hydrogen transfer from a sacrificial alcohol. In the case of Guerbet coupling, an MPV-like hydrogenation of adsorbed intermediate crotonaldehyde by ethanol would produce crotyl alcohol and acetaldehyde. This type of hydrogen transfer reaction was shown to occur rapidly over HAP by Kibby and Hall[43] many years ago. In that work, 2-butanol-2d$_1$ was reacted with 3-pentanone to form 3-pentanol-3d$_1$ at 423 K. Moteki and Flaherty[23] used isotope experiments to show that MPV-like hydrogen transfer saturates the C=O bond of butanal over HAP. Those authors claimed that the C=C bond of crotyl alcohol was hydrogenated by surface hydrogen. Although there are excellent studies of hydrogen transfer reactions, it is still unclear if the sacrificial alcohol transfers hydrogen directly to the carbonyl group, or if this hydrogen transfer is mediated by the catalyst surface.

Prior work on the Guerbet coupling of ethanol suggest that the reaction is autocatalytic, during which butanol is produced in great excess beyond the small amount of acetaldehyde produced by dehydrogenation of ethanol to produce H_2[22,23]. However, if ethanol provides H atoms to hydrogenate adsorbed intermediates produced from aldol condensation, then intermediate acetaldehyde is produced in the appropriate stoichiometric amount. The direct MPV-like hydrogen transfer from ethanol to adsorbed crotonaldehyde starts a reaction cascade that will result in the eventual production of one molecule of 1-butanol together with the formation of two molecules of acetaldehyde that were consumed in the aldol condensation reaction.

The role of surface hydrogen in hydrogenation reactions of alkenes has also been studied[2,5,23]. For example, ethene hydrogenation can occur on MgO that has been thermally treated at very high temperatures (>1000 K)[2,4,5,44]. The reaction occurs on sites capable of heterolytically dissociating H_2 that are exposed during the high temperature treatment. A surface hydride attacks the adsorbed olefin resulting in a carbanion that is subsequently protonated by a surface proton[7]. While this reaction can take place under temperatures relevant to Guerbet coupling, it was also shown that the introduction of water to the thermally-treated MgO destroys the sites that are active for heterolytic hydrogen dissociation[44].

Other reactions that involve surface hydrogen have also been studied on basic metal oxides, namely 1-butene isomerization and H_2-D_2 exchange. The isomerization reaction is thought to occur through the abstraction of an allylic hydrogen resulting in an allyl anion. This anion is then protonated by a surface proton resulting in a mixture of 1-butene, cis-2-butene, and trans-2-butene[7]. Since crotyl alcohol has a similar electronic structure to butene, it is feasible that

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on basic metal oxides double bond isomerization could produce an enol, which would rapidly tautomerize to adsorbed butanal. The H_2-D_2 exchange reaction was studied by Boudart et al.[8] who demonstrated exchange occurs at 78 K on MgO that was thermally-activated between 773 and 1173 K in vacuum. The proposed mechanism for H_2-D_2 exchange on MgO involves reaction of molecularly-adsorbed D_2 with a surface hydroxyl group through a triangular transition state. Unlike the case of olefin hydrogenation on MgO, hydride is not present during the exchange reaction.

In an attempt to better understand the role of hydrogen transfer reaction on the Guerbet coupling reaction, this paper investigates relevant hydrogenation and dehydrogenation reactions over HAP and MgO. In particular, benzyl alcohol dehydrogenation was chosen as a probe reaction because it has an α-hydrogen, which allows the dehydrogenation reaction to occur, but it does not have a β-hydrogen, which prevents aldol condensation of the aldehyde product. Preventing aldol condensation is important because higher levels of aldehyde formation would be measured if the alcohol is being oxidized during an MPV-like reaction with the aldol condensation product. Hydrogenation of acetone with either H_2 or ethanol was evaluated over HAP and MgO to explore the relative importance of MPV-like hydrogen transfer on the catalysts. In addition, the rate of the H_2-D_2 exchange reaction as well as the effect of H_2 or D_2 on the Guerbet coupling of ethanol over HAP and MgO were evaluated.

2. Materials and Methods

2.1 Catalyst Synthesis

Hydroxyapatite was synthesized using a co-precipitation method originally developed by Tsuchida et al.[45] and described in previous works[24,29]. A 200 cm^3 solution of 0.5 M calcium nitrate tetrahydrate ($Ca(NO_3)_2 \bullet 4H_2O$, Acros Organics) and a 200 cm^3 solution of 0.3 M diammonium phosphate ($(NH_4)_2HPO_4$, Aldrich, >99.99%) were slowly added to 100 cm^3 of distilled, deionized (DDI) water at 353 K. The slurry was aged over night before being filtered and washed three times with DDI water. The solid was subsequently dried in air at 373 K before being thermally treated at 673 K for 2 h in flowing air.

Commercially-available MgO was purchased from Ube Material Industries (Lot No. 109071725) and was thermally treated at 673 K for 2 h in flowing air. The particles of both HAP and MgO were sized between 106-180 µm prior to catalysis.

2.2 Catalyst Characterization

Phase purity was determined using XRD with a PANalytical X'Pert Pro diffractometer using Cu-Kα radiation. These materials have been used in previous studies and XRD patterns can be found elsewhere[29].

Elemental analysis of HAP was performed by Galbraith Laboratories (Knoxville, TN) using ICP-OES. The catalyst was found to be very nearly stoichiometric with a measured Ca/P = 1.67.

The catalyst surface area was determined with N_2 using the BET adsorption method on a Micromeritics ASAP 2020 at liquid N_2 temperature. Both HAP and MgO had a surface area of 35 $m^2\,g^{-1}$.

2.3 Catalytic Reactions

2.3.1 Guerbet Coupling in the Presence of H_2/D_2

Guerbet coupling was carried out in the presence of both H_2 (GTS-Welco, 99.999%) and D_2 (GTS-Welco, 99.7%) to determine if gas phase or surface hydrogen could be incorporated into the product. These isotopic studies were carried out using a downward-flow, fixed-bed, ¼" O.D. stainless steel reactor that was connected to an on-line mass spectrometer and an on-line gas chromatograph (GC). The catalyst bed (HAP or MgO) was supported in the reactor on quartz wool and was thermally treated in 50 $cm^3\,min^{-1}$ flowing argon (GTS-Welco, 99.999%) at 773 K prior to the reaction. Ethanol (Sigma-Aldrich, 99.5%) was introduced to the feed by flowing H_2 through a saturator at room temperature. The ethanol/H_2 stream was then passed over the catalyst. After the reaction came to steady-state, fifteen mass spectra of the product stream were collected. The carrier gas flowing through the saturator was then switched to D_2 and allowed to pass over the catalyst for 1 h before reaction rates were measured using an online GC equipped with a flame ionization detector and a Restek MXT-Q-Bond column (0.53 mm i.d., 30 m length). Subsequently, fifteen mass spectra were collected. Finally, the carrier gas was switched to He and the ethanol conversion rates were measured. A small amount of methane was introduced to the reactant stream to serve as an internal standard.

Product selectivity and conversion were calculated as

$$Selec. = \frac{N_i n_i}{\sum N_i n_i}$$

$$Conv. = \frac{\sum N_i n_i}{2 n_{EtOH}}$$

where N_i is the number of carbons in the product, n_i is the molar flow rate of the product, and n_{EtOH} is the molar flow rate of the reactant ethanol.

2.3.2 H_2-D_2 Exchange

The H_2-D_2 exchange reaction was performed in the same reactor as described above for the Guerbet coupling in the presence of H_2/D_2. During these reactions, an equimolar mixture of H_2 and D_2 was diluted in Ar. The partial pressure of the equimolar H_2/D_2 reaction mixture was varied while the total pressure was maintained at 1 atm. The catalyst bed (either HAP or MgO) was supported on quartz wool and was pretreated at 773 K in 100 $cm^3\,min^{-1}$ Ar for 1 h prior to the reaction. The H_2/D_2/Ar mixture was then passed over the catalyst at room temperature and the product stream was analyzed using a mass spectrometer measuring m/z=2,3,4 and 40.

2.3.3. Benzyl Alcohol Dehydrogenation

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A downward-flow, fixed-bed, ¼" O.D. stainless steel reactor with an on-line GC was used for the benzyl alcohol dehydrogenation reaction. The catalyst bed was supported on quartz wool and was pretreated at 773 K for 1 h in 100 cm^3 min^{-1} N_2 (GTS-Welco, 99.999%) prior to reaction. Pure benzyl alcohol (Sigma-Aldrich, 99.8%) was introduced to the system with a syringe pump and was vaporized in a high temperature mixing chamber together with flowing N_2. A small amount of methane (1 cm^3 min^{-1}) was added to the product stream downstream of the reactor as an internal standard. The reaction products were analyzed with an on-line gas chromatograph using a PoraPLOT Q-HT column and a flame ionization detector.

2.3.4 Hydrogenation of Acetone and Ethene

The same flow reactor and catalyst pretreatment conditions described for the benzyl alcohol dehydrogenation reaction were used for the hydrogenation reactions. When acetone was hydrogenated using ethanol as a hydrogen source, a 95 wt% ethanol, 5 wt% acetone (Sigma-Aldrich, 99.9%) solution was fed to the high temperature mixing chamber together with flowing N_2.

When ethene was hydrogenated using ethanol as a hydrogen source, a N_2/ethene (ethene from GTS Welco 99.5 %, 4 kPa ethene, 1 atm total pressure) gas mixture was passed through the high temperature mixing chamber with a 95 wt% ethanol/5 wt% octane solution. Octane was used as an internal standard.

To explore the reaction of acetone with H_2, pure H_2 carrier gas was passed through an acetone saturator that was submerged in a dry ice/acetone bath, which should produce 0.02 % acetone in H_2. Methane was introduced downstream of the reactor as an internal standard. For ethene hydrogenation with H_2 a mixture of ethene/H_2 feed (4 kPa ethene, 1 atm total pressure) was passed over the catalyst.

3. Results and Discussion

3.1 Guerbet Coupling in the Presence of H_2/D_2

Dihydrogen is a byproduct that can be produced during the Guerbet coupling reaction by alcohol dehydrogenation. Although H_2 is not a product of the coupling of ethanol into butanol, one molecule of H_2 is produced for every molecule of acetaldehyde, which is a common side product during the Guerbet coupling reaction. Our group and others have shown that adding gaseous H_2 has no effect on the rate of the ethanol coupling reaction or the selectivity towards butanol over HAP[23,41,42]. These observations do not preclude the possibility that H_2 interacts with the catalyst surface and can incorporate into product molecules. To explore this, the Guerbet coupling of ethanol was performed in the presence of dideuterium gas. The rate of ethanol conversion using He, H_2, or D_2 as a diluent are shown in Table 1. The Guerbet reaction was carried out at low conversion in all cases (≤ 5%). Both the rate and selectivity were relatively unaffected by the presence of H_2 or D_2. This similarity in rate and selectivity among H_2, D_2, and He as a diluent gas over each catalyst is consistent with previous reports showing a negligible influence of H_2 on coupling kinetics. Moreover, there is no kinetic isotope effect involving H_2 and D_2.

The mass spectra of butanol produced over HAP and MgO in H_2 and D_2 diluent gas are shown in Figure 1. For butanol production over HAP, the mass spectrum changes very little after the switch from H_2 to D_2. In contrast, the intensity of the butanol peaks at m/z = 57 and 58 increases significantly when MgO was used as the catalyst, indicating a fraction of D_2 from the gas phase incorporates into the butanol product, although there is no kinetic influence of D_2 on the reaction. Incorporation of deuterium into butanol can result from direct hydrogenation of C=C and/or C=O by D_2 or exchange of deuterium with surface bound hydrogen atoms that eventually incorporate into butanol. From the mass spectrum in Figure 1B, we estimate that 31% of the butanol had no deuterium, whereas 36%, 27%, and 6% had one D, two D, and three D atoms substituted into butanol, respectively. The lack of deuterium incorporation into the product butanol produced over HAP suggests that direct hydrogenation of C=C or C=O bonds of intermediate crotonaldehyde using H_2 as a hydrogen source does not take place to any significant extent.

The significant difference in the isotopomer distribution of butanol produced over HAP and MgO motivated a study of the H_2-D_2 exchange reaction as shown in Scheme 3. The MgO catalyst is known to be very active for this reaction at low temperatures[8,16]. Indeed, we observed the H_2-D_2 exchange reaction occurred readily at 298 K on MgO with a rate of 1.3 x 10^{-5} mol m^{-2} s^{-1} when the H_2 partial pressure was 2 kPa. The reaction was so rapid that conversion was ~30 % at all pressures tested, which is 83 % of the calculated equilibrium conversion for the reaction (f_{eq} = 36 %, K_{eq} = 3.2)[46]. The rate of H_2-D_2 exchange reported by Boudart et al.[8] measured at 78 K for an MgO sample calcined at ~650 K can be extrapolated to 298 K and 2 kPa H_2 using their reported activation energy. The extrapolated rate from Boudart et al.[8] of ~1.5 x 10^{-5} mol m^{-2} s^{-1} is similar to our measured rate and this agreement suggests that the MgO catalyst used in the current study exposes similar active sites for H_2-D_2 exchange as the catalyst prepared by Boudart et al.[8] They suggest the reaction proceeds through an Eley-Rideal like mechanism in which a proton on the catalyst surface reacts with a weakly adsorbed D_2 molecule through a triangular transition state[8] to produce a surface deuteron and gas phase HD. For our work on Guerbet coupling of ethanol, we suggest the surface deuteron produced via surface exchange with the D_2 could then add to a carbanion that is formed during the coupling reaction sequence. In this way, deuterium can incorporate into product butanol.

As no H_2-D_2 exchange was observed over the HAP catalyst at 298 K, it is not surprising that no deuterium is incorporated into butanol during Guerbet coupling of ethanol.

3.2 Hydrogenation Reaction

Results described in the previous section indicate that neither HAP nor MgO are able to directly hydrogenate C=C or C=O bonds of reactive intermediates formed during Guerbet coupling using gas phase H_2. Potential reactions of ethene and

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acetone in the presence of H_2 were then examined to further probe the hydrogenating ability of the catalyst. No 2-propanol was formed when H_2 and acetone were co-fed over either catalyst at 473 K. However, C_6 products were observed at 473 K due to the self-aldol condensation of acetone. When ethene and H_2 were passed through a blank reactor at 473 K containing no catalyst, a small amount of ethane was observed (~3 % ethene conversion). This background hydrogenation reaction was most likely catalyzed by the stainless-steel reactor. When the reaction was carried out in the presence of HAP and MgO, no conversion of ethene above the background was observed. The hydrogenation of ethene by H_2 over MgO has been previously reported to occur over catalysts that had been pretreated at very high temperatures (>1000 K)[4,5,44]. Formation of strong basic sites that were capable of heterolytically dissociating H_2 was proposed to account for the need of high temperature treatment. The hydride that was formed during the heterolytic dissociation then attacks the olefin resulting in a carbanion that would be subsequently protonated[7]. The milder pretreatment condition used to activate the MgO in the current study is apparently unable to form sites that are active for olefin hydrogenation. It should be noted, however, the background hydrogenation rates that were observed in our reactor are an order of magnitude greater than the hydrogenation rates that were reported in the previous studies[4]. As such, it is impossible for us to completely rule out the possibility that some C=C bonds of reactive intermediates produced during Guerbet coupling are being hydrogenated by these catalysts. Based on the lack of deuterium incorporation into butanol over HAP (Figure 1), it seems unlikely that a H_2/D_2 heterolytic dissociation is kinetically relevant. Additionally, the presence of water was shown previously to destroy the strongly basic sites required for heterolytic H_2 dissociation. Because water is a product of Guerbet coupling, it is unlikely that these sites would exist under Guerbet coupling conditions.

A commonly-proposed path for C=O hydrogenation involves an MPV-like mechanism[22,23] where hydrogen is transferred directly from a sacrificial alcohol to the C=O bond. Therefore, hydrogenation of C=O and C=C bonds using ethanol as a hydrogen source was also tested. In the case of ethanol reacting with crotonaldehyde, this would result in the formation of acetaldehyde and crotyl alcohol. To explore this type of transfer hydrogenation, the reaction of acetone to 2-propanol was performed over both HAP and MgO at 473 K using ethanol as the sacrificial alcohol as shown in Scheme 4. When excess ethanol was co-fed with acetone, the formation of 2-propanol was observed over both HAP and MgO, and Figure 2 shows the rate of 2-propanol formation at a constant ratio of acetone to ethanol diluted in N_2. Deactivation was observed over both HAP and MgO, which makes a direct comparison of rates difficult, but it is clear that both catalysts are able to hydrogenate acetone using ethanol as a hydrogen source. Over MgO, some C_6 products were observed and more acetaldehyde was produced than 2-propanol over this catalyst. No C_6 products were observed over HAP and a similar amount of acetaldehyde and 2-propanol were observed. It is possible that the excess acetaldehyde that was observed during the reaction over MgO is due to either background dehydrogenation of ethanol to acetaldehyde or to the transfer hydrogenation of C_6 carbonyl compounds produced by aldol condensation of acetone.

When ethene and ethanol were passed over both HAP and MgO at 473 K, no ethane formation was observed, indicating C=C bonds were not readily hydrogenated by either ethanol or H_2 under our reaction conditions. This observation suggests that the hydrogenation of intermediate crotonaldehyde proceeds through MPV-like alcohol transfer hydrogenation of the C=O bond to form crotyl alcohol, followed by a double bond isomerization reaction and keto/enol tautomerization to form butanal, and final MPV-like C=O bond hydrogenation to form the saturated alcohol 1-butanol. The double bond isomerization of butene will take place at water-ice temperatures over MgO[47] and we have shown that enolate formation occurs rapidly during the aldol condensation of acetaldehyde[29] indicating that both of these reactions will be very rapid for temperatures relevant to Guerbet coupling. This sequence of transfer hydrogenations from ethanol will produce two molecules of acetaldehyde that can undergo an aldol condensation step to regenerate the crotonaldehyde that was converted to butanol. The proposed reaction path is consistent with the autocatalytic mechanism that was proposed by Ho et al.[22]

The MPV-like C=O bond hydrogen transfer reaction was also proposed by Ogo et al.[42] and Moteki and Flaherty[23]. In the study by Ogo et al.[42] crotonaldehyde was reacted with both H_2 and 2-butanol present as a hydrogen source, and the authors found that H_2 was unable to hydrogenate crotonaldehyde at 573 K over a strontium substituted HAP, while the reaction between 2-butanol and crotonaldehyde lead to similar products as the overall Guerbet coupling of ethanol. Moteki and Flaherty[23] studied butanal and crotyl alcohol hydrogenation in the presence of fully deuterated 2-propanol and t-butanol with four times as much t-butanol present as 2-propanol-d_8. In this way, the surface of the catalyst will be populated in both hydrogen and deuterium due to the decomposition of adsorbed alcohols into alkoxides. The three to one ratio of unlabeled t-butanol to fully deuterated 2-propanol will result in a surface that has a three to one ratio of hydrogen to deuterium. If the hydrogenation reaction takes place predominantly through direct hydrogen transfer from deuterated 2-propanol the mass spectrum of the product will be shifted 1 amu. In contrast, if hydrogen originates from the surface, there will not be a shift in the mass spectrum. During the reaction of butanal under these conditions there was a 1 amu shift in the butanol mass spectrum indicating that a deuterium atom was transferred directly from 2-propanol-d_8 to butanal. Interestingly, the hydrogenation of crotyl alcohol with 2-propanol-d_8 did not shift the mass spectrum of the product butanol, which lead the authors to conclude that the C=C bond of crotyl alcohol was hydrogenated by a surface hydrogen atom. The conclusion that C=C is hydrogenated is not supported by the results of the current work and

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additional studies are underway to understand the nature of this inconsistency.

The observation by Moteki and Flaherty that there is almost no deuterium incorporation while hydrogenating the two carbon atoms in the C=C of crotyl alcohol in the presence of 20% D coverage on the surface is intriguing. Since the overall hydrogenation reaction should involve the simultaneous dehydrogenation of deuterated 2-propanol (t-butanol cannot dehydrogenate), the lack of appearance of any D in the product indicates there is significant H-D exchange with the surface on the time scale of the reaction. If the crotyl alcohol in the Moteki and Flaherty experiment undergoes the double bond isomerization and keto-enol tautomerization as proposed in our work, the final C=O hydrogenation reaction may involve surface H atoms.

3.3 Benzyl Alcohol Dehydrogenation

Although an autocatalytic cycle that converts ethanol to butanol is consistent with Guerbet coupling kinetics, formation of acetaldehyde via dehydrogenation must also take place to initiate the autocatalytic sequence. To study this initiation reaction, the dehydrogenation of benzyl alcohol, shown in Scheme 5, was performed. The dehydrogenation of benzyl alcohol occurred readily over both HAP and MgO with little deactivation and no observed side products. Figure 3 shows the rate of reaction over both HAP and MgO at 633 K and different alcohol partial pressures. The MgO catalyst was more active on an area basis for alcohol dehydrogenation than HAP. The rate of reaction is fit well by a Langmuir-Hinshelwood rate equation derived from a two-step model consisting of equilibrated dissociative adsorption of the alcohol followed by a rate determining unimolecular surface reaction, which is most likely C-H bond activation of the adsorbed alkoxide intermediate. This is consistent with an E_{1cB} mechanism that has been proposed elsewhere[40].

Over MgO, the rate of benzyl alcohol dehydrogenation is higher than the rate of Guerbet coupling of ethanol, despite the benzyl alcohol reaction being carried out 40 K lower, which may result from the presence of the aromatic ring. No Guerbet coupling of ethanol was observed over MgO at 633 K with similar contact times. Over HAP, the rate of benzyl alcohol dehydrogenation (Figure 3) is lower than the overall rate of ethanol Guerbet coupling shown in Table 1 despite the dehydrogenation reaction being carried out at a temperature 20 K higher and the higher reactivity of benzyl alcohol compared to ethanol. Both the dehydrogenation of benzyl alcohol and the Guerbet coupling of ethanol were carried out under conditions where the reaction is near zero order as shown in Figure 3 for benzyl alcohol dehydrogenation and the work of Hanspal et al.[41] for the Guerbet coupling of ethanol. Evidently, a significant portion of intermediate acetaldehyde that proceeds to form butanol during Guerbet coupling of ethanol over HAP is not formed by direct dehydrogenation of ethanol to acetaldehyde and H_2. Instead, the MPV-like transfer of hydrogen from ethanol to adsorbed intermediates must be responsible for production of most of the acetaldehyde.

4. Conclusions

The addition of H_2 or D_2 to the Guerbet coupling of ethanol over HAP and MgO had no effect on rate or selectivity of the reaction toward butanol. The partial incorporation of deuterium into the product butanol produced over MgO is attributed to the deuteration of the hydroxyls of MgO through rapid exchange with D_2. Indeed, rapid H_2-D_2 exchange occurred on MgO at room temperature but was not observed on HAP. Both MgO and HAP catalyzed the MPV-like hydrogen transfer from ethanol to acetone at 473 K, but neither catalyst could hydrogenation acetone with H_2. The hydrogenation of ethene to ethane was not observed above background conversion at 473 K using H_2 and ethanol as hydrogen sources. Evidently, all of the hydrogen transfer reactions during Guerbet coupling involve MPV-like reactions between alcohols and carbonyls. No evidence for C=C hydrogenation was observed, which suggests hydrogenation via MPV-hydrogen transfer steps likely undergo a double bond shift to form an enol, which is tautomerized to a carbonyl. The rate of benzyl alcohol dehydrogenation was lower than the rate of ethanol coupling over HAP, consistent with MPV-like conversion of ethanol to acetaldehyde being a major source of the acetaldehyde needed to form butanol.

Conflicts of Interest

There are no conflicts of interest to declare.

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Notes and references

(1) Hattori, H.; Tanaka, Y. *J. Am.* **1976**, *4652* (3), 4652–4653.
(2) Tanaka, Y.; Hattori, H.; Tanabe, K. *Chem. Lett.* **1976**, 37–38.
(3) Claus, P. *Appl. Catal. A Gen.* **2005**, *291* (1–2), 222–229.
(4) Tezuka, M.; Inoue, Y.; Yasumori, I. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2515.
(5) Hattori, H.; Tanaka, Y.; Tanabe, K. *Chem. Lett.* **1975**, 659–660.
(6) Bordawekar, S. V.; Davis, R. J. *J. Catal.* **2000**, *189* (1), 79–90.
(7) Hattori, H. *Chem. Rev.* **1995**, *95*, 537–558.
(8) Boudart, M.; Delbouille, A.; Derouane, E. *J. Am. Chem. Soc.* **1972**, *2312* (6), 6622–6630.
(9) Augustine, R. L.; Yaghmaie, F.; Peppen, J. F. Van. *J Org Chem* **1984**, No. 10, 1865–1870.
(10) Kozlowski, J. T.; Davis, R. J. *ACS Catal.* **2013**, *3* (7), 1588–1600.
(11) Gabriels, D.; Hernandez, W. Y.; Sels, B.; Van Der Voort, P.; Verberckmoes, A. *Catal. Sci. Technol.* **2015**, *5* (8), 3876–

View Article Online
DOI: 10.1039/C7CY01393K

3902.

(12) Savage, N. *Nature* **2011**, *474* (7352), S9–S11.

(13) Chieregato, A.; Velasquez Ochoa, J.; Bandinelli, C.; Fornasari, G.; Cavani, F.; Mella, M. *ChemSusChem* **2015**, *8* (2), 377–388.

(14) Birky, T. W.; Kozlowski, J. T.; Davis, R. J. *J. Catal.* **2013**, *298*, 130–137.

(15) Ndou, A. S.; Plint, N.; Coville, N. J. *Appl. Catal. A Gen.* **2003**, *251* (2), 337–345.

(16) Di Cosimo, J.; Apesteguía, C.; Ginés, M.; Iglesia, E. *J. Catal.* **2000**, *190* (2), 261–275.

(17) Ordóñez, S.; Díaz, E.; León, M.; Faba, L. *Catal. Today* **2011**, *167*, 71–76.

(18) León, M.; Diaz, E.; Ordóñez, S. *Catal. Today* **2010**, *164*, 436–442.

(19) Yang, C.; Meng, Z. Y. *J. Catal.* **1993**, *142* (1), 37–44.

(20) Tsuchida, T.; Sakuma, S.; Takeguchi, T.; Ueda, W. *Ind. Eng. Chem. Res.* **2006**, *45* (25), 8634–8642.

(21) Ogo, S.; Onda, A.; Yanagisawa, K. *Appl. Catal. A Gen.* **2011**, *402* (1–2), 188–195.

(22) Ho, C. R.; Shylesh, S.; Bell, A. T. *ACS Catal.* **2016**, *6*, 939–948.

(23) Moteki, T.; Flaherty, D. W. *ACS Catal.* **2016**, *6* (7), 4170–4183.

(24) Hanspal, S.; Young, Z. D.; Shou, H.; Davis, R. J. *ACS Catal.* **2015**, *5*, 1737–1746.

(25) Carlini, C.; Di Girolamo, M.; Macinai, A.; Marchionna, M.; Noviello, M.; Raspolli Galletti, A. M. R.; Sbrana, G. *J. Mol. Catal. A-Chem.* **2003**, *200* (1–2), 137–146.

(26) Carlini, C.; Girolamo, M. D.; Marchionna, M.; Noviello, M.; Galletti, A. M. R.; Sbrana, G. *J. Mol. Catal. A Chem.* **2002**, *184* (1–2), 273–280.

(27) Ndou, a. S.; Coville, N. J. *Appl. Catal. A Gen.* **2004**, *275* (1–2), 103–110.

(28) Scalbert, J.; Thibault-Starzyk, F.; Jacquot, R.; Morvan, D.; Meunier, F. *J. Catal.* **2014**, *311*, 28–32.

(29) Young, Z. D.; Hanspal, S.; Davis, R. J. *ACS Catal.* **2016**, *6*, 3193–3202.

(30) Rekoske, J. E.; Barteau, M. a. *Ind. Eng. Chem. Res.* **2011**, *50* (1), 41–51.

(31) Reichle, W. *J. Catal.* **1980**, *63* (2), 295–306.

(32) Di Cosimo, J. I.; Diez, V.; Apesteguia, C. *Appl. Catal. A Gen.* **1996**, *137* (1), 149–166.

(33) Sharma, S. K.; Parikh, P. a.; Jasra, R. V. *J. Mol. Catal. A Chem.* **2007**, *278* (1–2), 135–144.

(34) Luo, S.; Falconer, J. L. *J. Catal.* **1999**, *185* (2), 393–407.

(35) Raskó, J.; Kiss, J. *Appl. Catal. A Gen.* **2005**, *287* (2), 252–260.

(36) Wang, S.; Goulas, K.; Iglesia, E. *J. Catal.* **2016**, *340*, 302–320.

(37) Gines, M. J. L.; Iglesia, E. *J. Catal.* **1998**, *176*, 155–172.

(38) Carlini, C.; Flego, C.; Marchionna, M.; Noviello, M.; Raspolli Galletti, A. M.; Sbrana, G.; Basile, F.; Vaccari, A. *J. Mol. Catal. A Chem.* **2004**, *220* (2), 215–220.

(39) Carlini, C.; Marchionna, M.; Noviello, M.; Raspolli Galletti, A. M.; Sbrana, G.; Basile, F.; Vaccari, A. *J. Mol. Catal. A Chem.* **2005**, *232* (1–2), 13–20.

(40) Diez, V. K.; Apesteguía, C. R.; Di Cosimo, J. I. *Catal. today* **2000**, *63* (1), 53–62.

(41) Hanspal, S.; Young, Z. D.; Prillaman, J. T.; Davis, R. J. *J. Catal.* **2017**, *352*, 182–190.

(42) Ogo, S.; Onda, A.; Iwasa, Y.; Hara, K.; Fukuoka, A.; Yanagisawa, K. *J. Catal.* **2012**, *296*, 24–30.

(43) Kibby, C. L.; Hall, W. K. *J. Catal.* **1973**, *31* (Copyright (C) 2014 American Chemical Society (ACS). All Rights Reserved.), 65–73.

(44) Inoue, Y.; Yasumori, I. *Bulletin of the Chemical Society of Japan*. 1981, pp 1505–1510.

(45) Tsuchida, T.; Kubo, J.; Yoshioka, T.; Sakuma, S.; Takeguchi, T.; Ueda, W. *J. Japan Pet. Inst.* **2009**, *52* (2), 51–59.

(46) Woolley, H. W.; Scott, R. B.; Brickwedde, F. G. *J. Res. Natl. Bur. Stand. (1934).* **1948**, *41* (5), 379–475.

(47) Fishel, C. T.; Davis, R. J. *Catal. Letters* **1994**, *25* (1), 87–95.

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Scheme 1. The overall Guerbet coupling reaction of ethanol to butanol and water.

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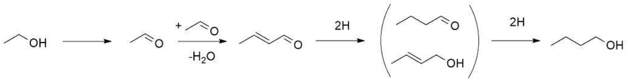
Scheme 2. The Guerbet coupling reaction network



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Scheme 3. The H_2-D_2 exchange reaction.

$$H_2 + D_2 \rightleftharpoons 2\,HD$$

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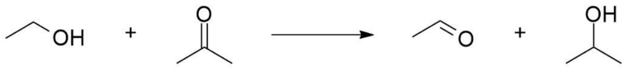
Scheme 4. The overall MPV-like hydrogen transfer reaction from ethanol to acetone.



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Scheme 5. Benzyl alcohol dehydrogenation.

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Table 1. Influence of H_2 or D_2 on Rate and Selectivity of Ethanol Conversion over HAP and MgO$^{(a)}$

Catalyst	T (K)	Diluent Gas	Ethanol Conversion Rate (mol m^{-2} s^{-1})	Butanol Selectivity (C%)
HAP	613	He	5.0×10^{-8}	65
HAP	613	H_2	6.4×10^{-8}	61
HAP	613	D_2	7.2×10^{-8}	63
MgO	673	He	2.5×10^{-8}	17
MgO	673	H_2	2.5×10^{-8}	23
MgO	673	D_2	2.7×10^{-8}	24

(a) Partial pressure of ethanol = 6 kPa, remainder diluent gas to give 101 kPa total pressure. All ethanol conversion levels were < 5%. Catalyst loading = 0.05 g for HAP and 0.2 g for MgO. Flow rate = 50 cm^3 min^{-1}.

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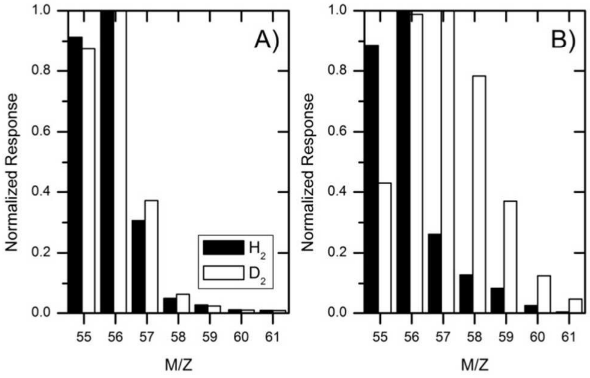

Figure 1. Mass spectra of the butanol carbon backbone over A) HAP and B) MgO during the Guerbet coupling reaction in the presence of H_2 or D_2 carrier gas.

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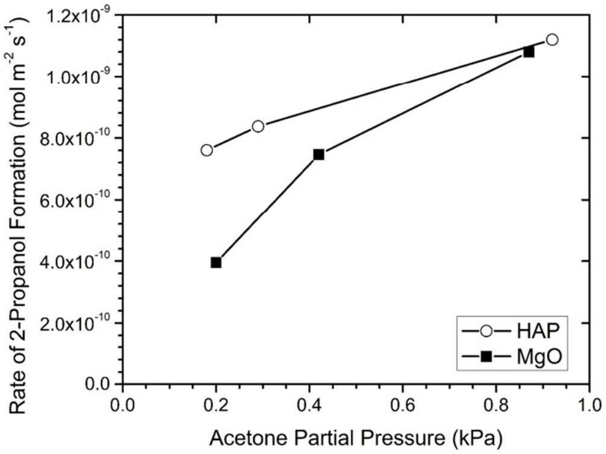

Figure 2. The rate of MPV-like hydrogenation over HAP and MgO at 473 K. The reaction was carried out at atmospheric pressure with an acetone to ethanol molar ratio of 0.07 at all acetone partial pressures. Catalyst loading = 0.2 g Flow rate = 25 cm^3 min^{-1}.

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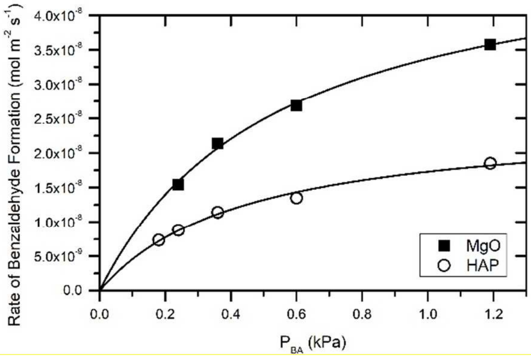

Figure 3. The rate of benzaldehyde formation over HAP and MgO at 633 K. The reaction was carried out at atmospheric total pressure with N_2 as a diluent gas. Catalyst loading = 0.05 g. Total flow rates were between 200 – 400 cm^3 min^{-1}.

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The rates of double bond hydrogenation, deuterium exchange, and benzyl alcohol dehydrogenation were compared to those of ethanol coupling.