



Catalytic Oxidative Dehydration of Butanol Isomers: 1-Butanol, 2-Butanol, and Isobutanol

by Ivan C. Lee, Jeffrey G. St. Clair, and Adam S. Gamson

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14. ABSTRACT The catalytic production of economically important four-carbon olefins was achieved through catalytic oxidative dehydration of 1-butanol, 2-butanol, and isobutanol using a millisecond contact time reactor. Both alumina foam and rhodium-alumina foam catalysts convert these four-carbon alcohols into four-carbon olefins, with contact time equal to 25 ms over a wide range of equivalence ratios (ϕ) from 0.176 to 6.338 (or C/O_{air} ratio from 0.0659 to 2.11). The cracking of the carbon backbone was found to be minimal. A mixture of butene isomers was obtained due to the isomerization of the carbocation intermediates. The degree of this isomerization was determined by analyzing the ratios of butenes/(total olefins), 1-butene/2-butene, cis-2-butene/trans-2-butene, and isobutene/(linear butenes). In addition, a reaction mechanism of the catalytic oxidative dehydration of butanol in short contact times was proposed. In this mechanism, the C-O bond of the majority of butanol was broken to form olefinic species on the alumina surface. These surface olefinic species would undergo successive oxidation to form CO and/or CO₂, depending on the availability of oxygen.					
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1. Introduction

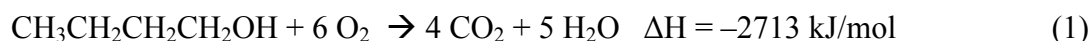
Butanol is a potential alternative hydrocarbon source for energy and chemical industries because it is easily available through fermentation of non-food biomass and wastewater (1–3).

Dehydration of butanol isomers (1-butanol, 2-butanol and isobutanol) produces butenes, such as 1-butene, cis-2-butene, trans-2-butene and isobutene, which are highly valuable starting materials for other industries to make synthetic fuels, lubricants, and other high value chemicals. For example, 1-butene is used in the creation of plastic materials, such as linear low density polyethylene. 2-butene isomers are an extremely valuable starting material for lubricants, as well as agricultural chemicals (4). In olefin metathesis, 2-butene reacts with ethylene to form propylene (5). Isobutene is the starting material for butyl rubber, methyl tert-butyl ether (MTBE), and isooctane. In addition, synthetic petroleum kerosene (SPK) can be synthesized by oligomerization of 4-carbon olefins (6–8).

The production of olefins from hydrocarbons, as well as other sources, such as biodiesel and C₁-C₃ alcohols, is well documented in the literature (9–12). In one such process, ethane auto-thermally decomposes to form ethylene (9). This process also converts heavier paraffins, such as n-octane, into mixtures of olefins (10). A rhodium/cerium catalyst has been proposed in the past to convert biodiesel into olefins (11). The catalyst produces mainly two- and three-carbon olefins, and has a total olefin selectivity of about 42%. The preferred contact time was no greater than 50 ms. In another work, Wanat et al. suggested that alkoxyl species was the surface intermediate for olefin production from C₁-C₃ alcohols (12).

A process for converting dry and aqueous 2-butanol directly to isooctenes was carried out in a batch process (13, 14). The butanol conversions were as high as 75%, but the product selectivity into the desired iso-octenes was generally very low, creating only a small product yield (yield = conversion × selectivity). The same group proposed another process of butene production from dry and aqueous 2-butanol in a pressurized batch reactor (15, 16). They were able to achieve 100% conversion and 100% selectivity of a 70 wt% mixture of butanol with sulfuric acid as a catalyst (16).

Recently, catalytic combustion of 1-butanol in a millisecond contact time reactor has been demonstrated (17). The combustion of 1-butanol is extremely exothermic and occurs via the process detailed in Equation 1.



This heat production enables the reaction to perform auto-thermally. As a result, the catalytic reaction initiates at a temperature as low as 240 °C, and the catalyst temperature rises to 450 °C or above. It was shown that three distinct regimes exist in the catalytic butanol combustion. The product selectivity can be tuned by changing the equivalence ratio (ϕ), which is the operating

fuel-to-air ratio compared to the stoichiometric value. When the equivalence ratio is less than 1, complete combustion occurs with the formation of H_2O and CO_2 as the major products. In the second regime of slightly higher equivalence ratios, the product selectivities of hydrogen (H_2) and carbon monoxide (CO) increase. Finally, further increase in equivalence ratio promotes the formation of olefins in an autothermal process. In contrast, traditional dehydration processes require external heating to maintain catalyst temperatures at about 300–400 °C (18, 19).

In this study, catalytic oxidative dehydration of three butanol isomers including 1-butanol, 2-butanol, and isobutanol was investigated in a short contact time reactor with residence time of 25 ms and a pressure drop of less than 10 psig. The product selectivity of each butanol isomer in a $\text{Rh}/\text{Al}_2\text{O}_3$, a $\gamma\text{-Al}_2\text{O}_3$ -coated alumina foam, a blank alumina foam, and an empty tube reactor were compared. Based on these results, contributions of homogenous and heterogeneous reactions were determined. Then a mechanism of the olefin production and consumption is proposed.

2. Experimental

2.1 Materials

Catalytic oxidative dehydration of 1-butanol, 2-butanol, and isobutanol was investigated using three catalysts and an empty reactor tube in this study. All three butanol isomers are of high performance liquid chromatography (HPLC) grade or higher. The primary catalyst was comprised of a $\text{Rh}/\text{Al}_2\text{O}_3$ foam as in previous studies [17, 22]. The catalyst preparation started with alumina monolith foam (Vesuvius, 80 ppi, 17 mm diameter, 1 cm thick) that was coated with γ -alumina to roughen the foam surface and increase the surface area. Then the foam was calcined in a box furnace at 700 °C for 15 h. An aqueous $\text{Rh}(\text{NO}_3)_3$ solution was added to the gamma-alumina coated foam, and the resultant foam was calcined in the box furnace at 700 °C for another 15 h. The resulting $\text{Rh}/\text{Al}_2\text{O}_3$ foam catalyst contained approximately 0.07353 g of Rh. The second catalyst is the γ -alumina coated foam without Rh. The third catalyst is a blank monolith foam. Lastly, the reaction was studied in an empty tube configuration.

2.2 Reactor Setup and Operation

The experimental set-up of the cylinder quartz reactor (2 cm diameter) is shown in figure 1. Amounts of nitrogen (N_2) and oxygen (O_2) gases were controlled with two separate MKS mass flow controllers, and the resultant mixture was introduced near the top of the reactor. An amount of liquid butanol was delivered through a 1/16 in stainless steel tubing from a VICI micropump. A grounded –tantalum (Ta) mesh and a mixing alumina foam (45 ppi) was placed 1 cm below the end of this fuel delivery tube. The catalyst material was placed between other two alumina foams (45 ppi) that acted as heat shields, and also served as another mixing layer to ensure uniform fuel vapor concentration over the entire catalyst surface. The distance between the

grounded mesh and the top heat shield was 12.5 cm, and this region was surrounded by heating tape to assist fuel vaporization and to preheat the catalyst material to the ignition temperature (240 °C for Rh/Al₂O₃ catalyst). The preheat temperature for the other three catalyst configurations was between 460–500 °C so that the final catalyst backface temperature was comparable to that of the Rh/Al₂O₃ (table 5 in supplementary materials).

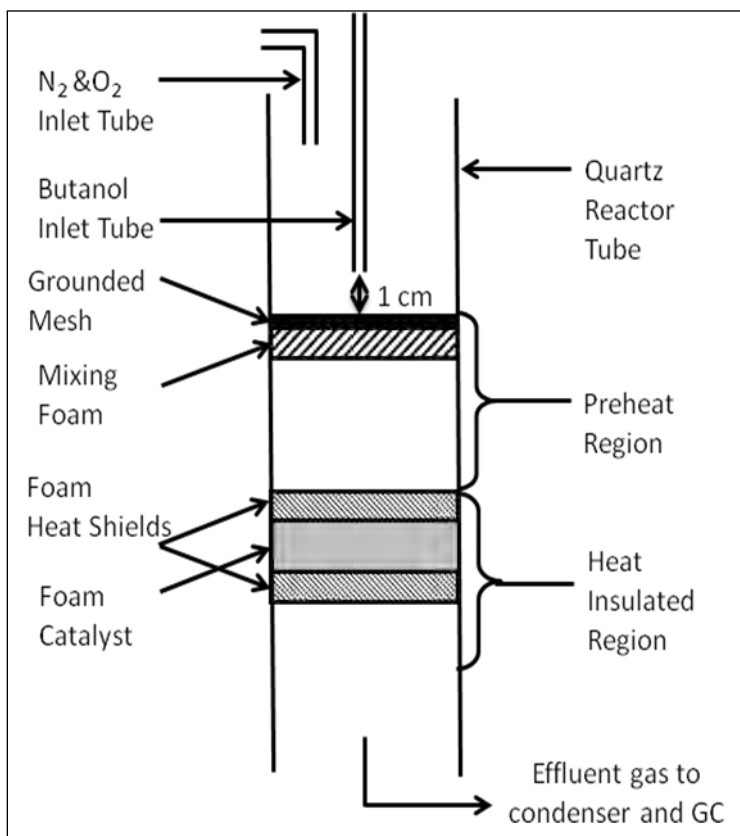


Figure 1. Experimental setup for olefin production.

Initially, the catalyst was preheated to the self-ignition temperature by flowing only N₂ and O₂ through the preheat region. Once the catalyst reached the self ignition temperature, the liquid fuel was electrosprayed in cone-jet mode by creating a voltage difference (~3300 V) between the droplet source and a neutral grounded mesh (17, 22). Once the catalyst was ignited, the catalyst backface temperature was allowed to reach its steady-state temperature. The effluent gas was sent to an ice-water bath, then to the Agilent 4-channel micro gas chromatograph (GC) for composition analysis.

2.3 Product Gas Analysis

The amounts of H₂, O₂, N₂, CO, carbon dioxide (CO₂), methane, acetylene, ethane, ethylene, propane, propylene, butane, 1-butene, cis-2-butene, trans-2-butene, isobutene, 1,3-butadiene, 1,2-butadiene, pentane, cis-2-pentene, and trans-2-pentene were monitored by an Agilent 4-channel micro-GC. Each analysis takes approximately 4 min, and 10 analyses were performed to obtain

the average gas composition. Conversion is defined by carbon balance (equation 2). When all the carbon atoms in butanol are converted to the carbon species—including CO, CO₂, methane, acetylene, ethane, ethylene, propane, propylene, butane, 1-butene, cis-2-butene, trans-2-butene, and isobutene—the conversion would be 100%. The carbon selectivity was defined as the number of carbon atoms in a product species, divided by the total number of carbon atoms in all the product species (equation 3).

$$\text{Conversion} = \frac{\sum C \text{ in } CO, CO_2, \text{Paraffin, Olefin Species}}{\sum C \text{ in Alcohol Feed}} \quad (2)$$

$$C \text{ atom Selectivity} = \frac{\#C \text{ in Species } X}{\sum C \text{ in product}} \quad (3)$$

The amounts of oxygenates from the oxidative dehydration of all three butanol isomers over the γ -Al₂O₃-coated foam were determined by analyzing exhaust gas composition with the flame ionization detector of a GC. A HP-INNOWAX column was employed to quantify polar molecules including 1-butanol, 2-butanol, isobutanol, other C₁-C₃ alcohols (methanol, ethanol, 1-propanol, 2-propanol), aldehydes (formaldehyde, acetaldehyde, propionaldehyde, isobutiraldehyde, butanal), and ketones (acetone, 2-butanone). It was found that the concentration of the C₁-C₃ alcohols, aldehydes, or ketones was less than 50 ppm, which corresponded to carbon selectivity of less than 0.05%.

2.4 Equilibrium Calculations of 1-butanol Conversion

Gas phase equilibrium calculations of 1-butanol combustion were carried out using the software Chemkin Pro Release 15092 from Reaction Design. Such calculations require only the thermodynamic properties of each compound considered for the simulation, thus no transport or kinetic properties are necessary. The thermodynamic data set originates from Sarathy et al. (20). The gas and fuel ratios are the same as those used for the reactor. Equivalent ratios from 0.18 to 6.34 were investigated using a constant temperature and pressure process. The temperature for each equivalence ratio matched the backface temperature of the alumina catalyst at that equivalence ratio (between 481 °C and 491 °C). The pressure was set at 1 atm. The software displays the mole fraction of each constituent of the resulting product gas. Selectivity was then calculated using the same methodology that was described in the previous section. By comparing the calculated equilibrium product selectivity with the experimental value, the effect of short contact time (25 ms) on reaction kinetics can be determined.

3. Results

3.1 Equilibrium Calculations

The carbon and H selectivity of 1-butanol homogeneous combustion that has reached equilibrium is given in figure 2. At low ϕ values, complete combustion is observed, in that only CO_2 and water are formed. CO and H_2 reached a maximum selectivity at $\phi = 3.5$, whereas CO_2 and water selectivities drop significantly as the equivalence ratio is increased. Methane, the other major product, increases in selectivity as the amount of O_2 relative to fuel decreases. Other compounds were observed, including olefins, but these compounds had negligible selectivities ($<0.1\%$).

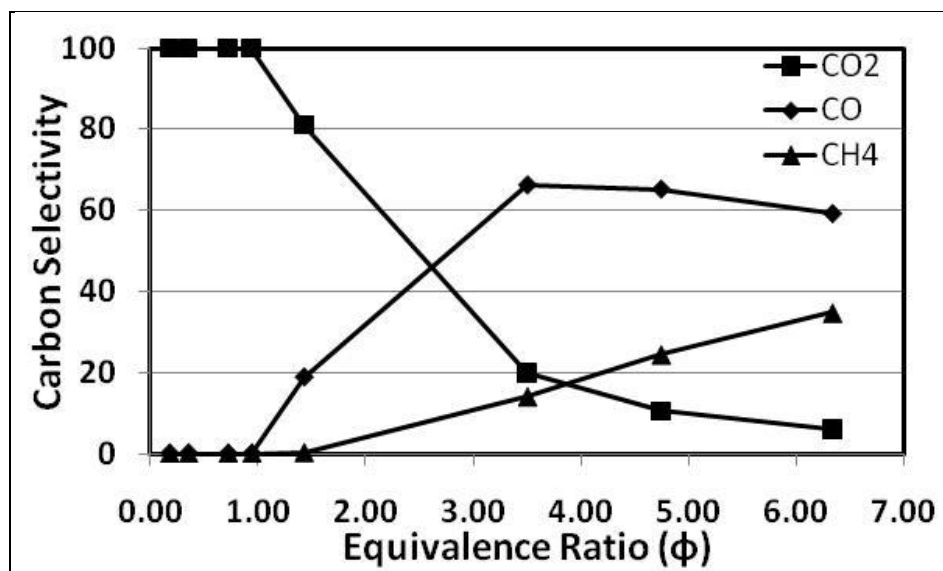


Figure 2. Equilibrium calculations of product selectivity for 1-butanol reaction with O_2 .

3.2 Conversion

Figure 3 illustrates the conversion of butanol isomers with four different catalyst configurations. The alcohol conversion with the empty tube remained small ($<25\%$). Conversions of isobutanol and 1-butanol were less than 10% for all equivalence ratios, while the conversion of 2-butanol was around 20%. This could suggest that 2-butanol is more reactive than the other two butanol isomers in gas phase conversion. In general, the conversion of butanol isomers increases as empty tube $<$ blank alumina foam $<$ γ -alumina coated foam $<$ Rh/alumina foam.

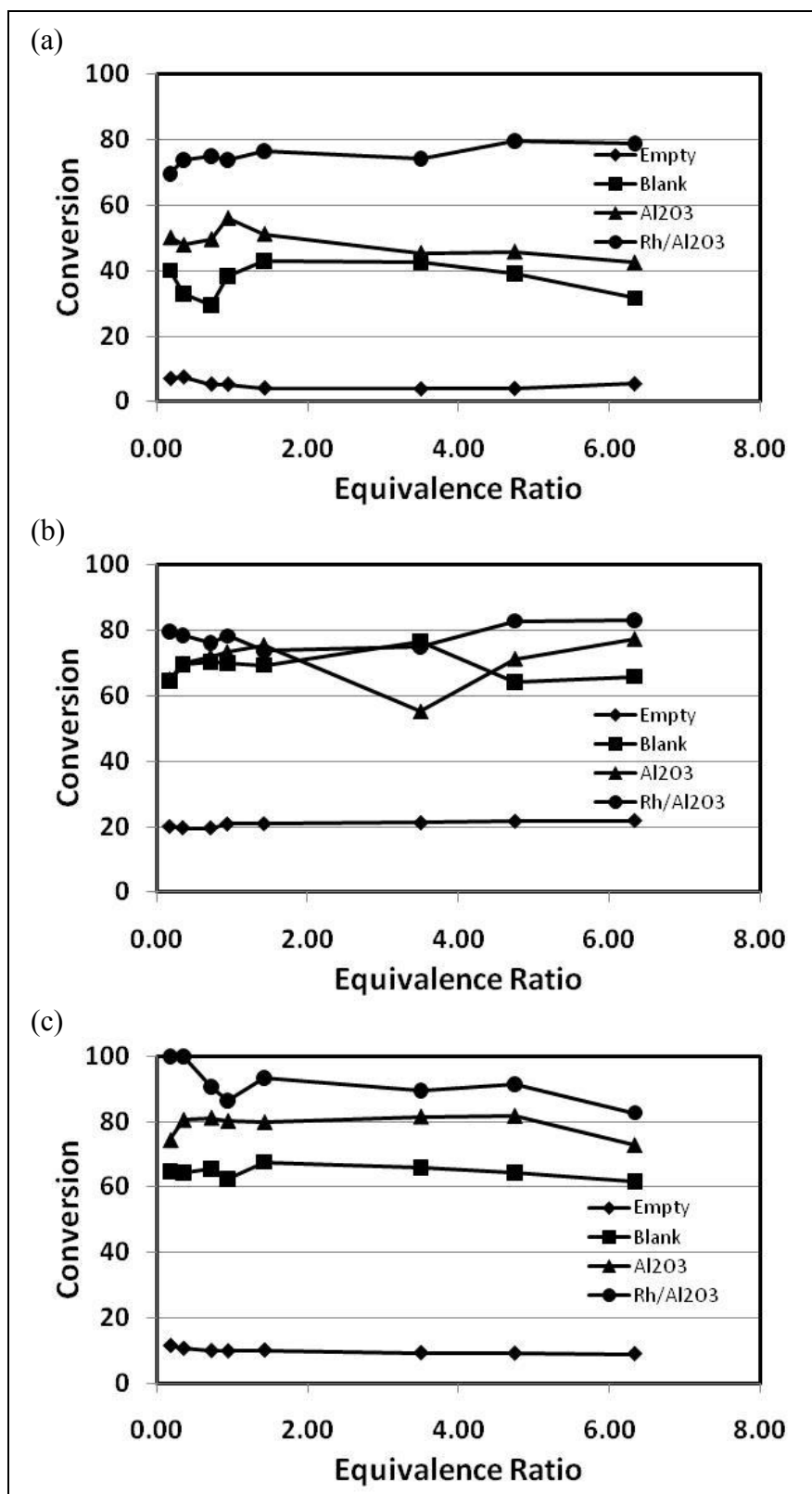


Figure 3. Conversion of butanol isomers with empty tube, blank alumina foam, γ -alumina coated foam, and Rh/alumina foam: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

3.3 Olefins Selectivity and Distribution

Figure 4 illustrates the carbon selectivity of catalytic oxidative dehydration of butanol isomers. In contrast to equilibrium calculations, olefin selectivity generally remains at a high level (>80%) at all equivalence ratios for configuration of empty tube, blank alumina foam, and γ -alumina coated foam. This suggested that the contact time of 25 ms was too short to crack the C-C bond in the butanol backbone. Cracking reaction will be discussed later. As previously mentioned, three distinct regimes exist in presence of Rh, and the reactor can be tuned to operate in any regime by changing the equivalence ratio. Increasing the equivalence ratio reduces the relative amount of O₂ in the feed. As is shown in figure 4, olefins selectivity started to increase after $\phi = 1.42$. At $\phi = 4.75$, the carbon selectivities of olefins from 1-butanol, 2-butanol, and isobutanol were 21.9, 21.6, and 29.0, respectively. Further increase of equivalence ratio enhances olefins production. At $\phi = 6.34$, the corresponding carbon selectivities of olefins were 39.7, 38.5, and 46.0, respectively.

The olefins distribution was analyzed by butenes/(total olefins) ratio, 1-butene/2-butene ratio, cis/trans ratio, and (isobutene)/(linear butane) ratio. These ratios for each isomer at all equivalence ratios were tabulated in the supplemental materials. It was observed that butenes/(total olefins) ratio was generally > 90% in absence of Rh with each butanol isomer at all equivalence ratios. The only exception was the 1-butanol reaction in an empty tube, in which the butenes/(total olefins) ratio was between 0.520 to 0.716 for $0.176 < \phi < 6.34$. In the empty tube configuration, ethylene and propylene were produced from 1-butanol. In the presence of Rh, the butenes / (total olefins) ratio for 1-butanol, 2-butanol, and isobutanol reactions were 0.874, 0.979, and 0.951, respectively.

The preferred butene product was different depending on the butanol isomer. The 1-butene/2-butene ratio for 1-butanol reaction was > 1 for all catalyst configurations at each ϕ , while the isobutene/(linear butenes) ratio was always equal to 0. These results indicate that 1-butene was the preferred butene product. In contrast, the 1-butene/2-butene ratio for 2-butanol reaction was <1 for all catalyst configurations at each ϕ , while the isobutene/(linear butenes) ratio was always equal to 0. The cis/trans ratio is >1. These indicated that cis-2-butene was the preferred butene product from 2-butanol reaction. Finally, the preferred butene product from isobutanol reaction was isobutene. The isobutene/(linear butenes) ratio was always >1. 1-butene/2-butene ratio was <1, except in the empty tube configuration.

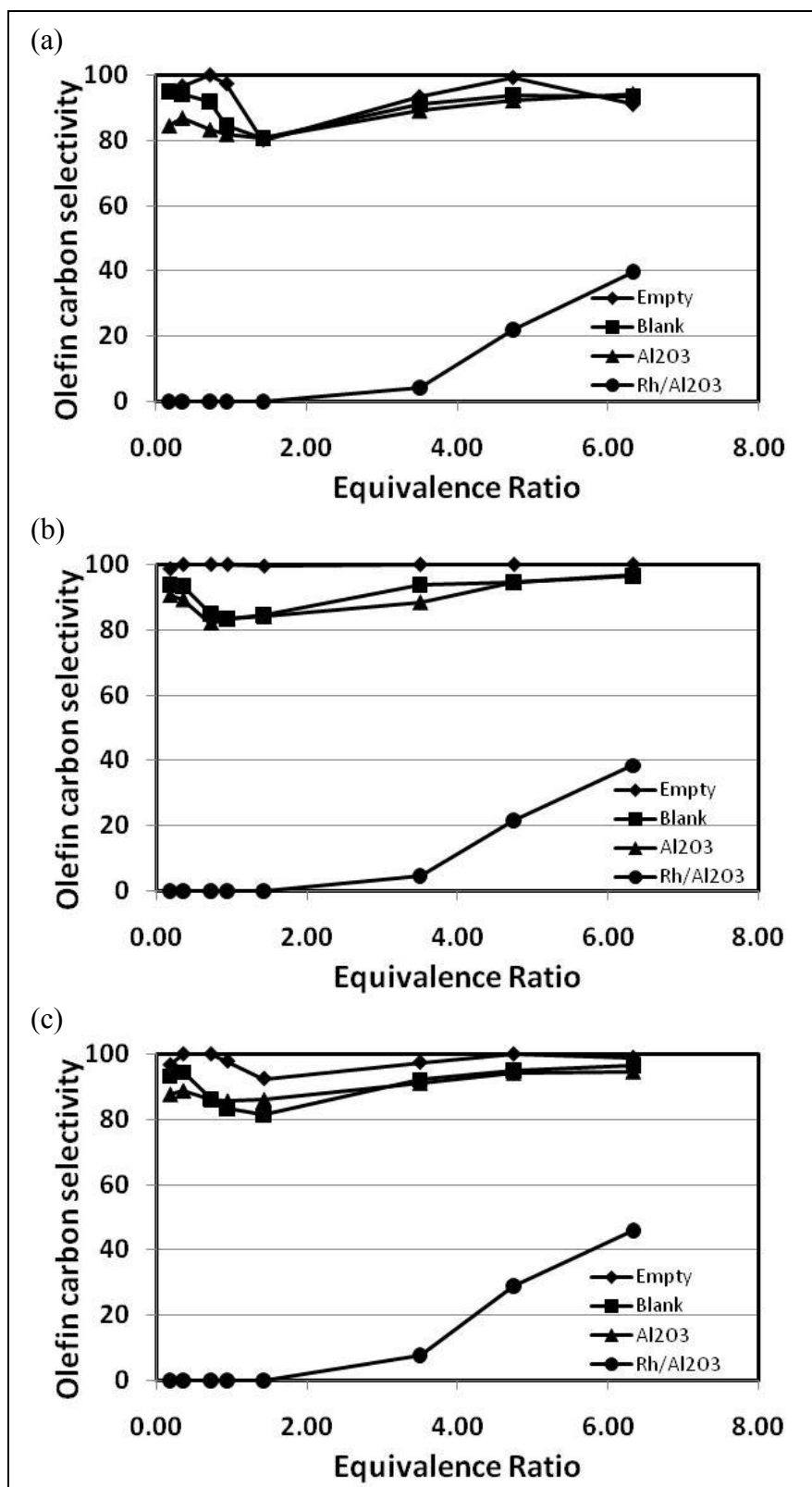


Figure 4. Olefins selectivity for catalytic oxidative dehydration of butanol isomers with empty tube, blank alumina foam, γ -alumina coated foam, and Rh/alumina foam: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

3.4 CO Selectivity

Figure 5 illustrates the CO selectivity from the reaction of each butanol isomer. In the absence of Rh, the CO selectivity remains low (<7 %). In contrast, the CO selectivity with a Rh/alumina catalyst started to rise at $\phi = 1.42$ and reached a maximum at $\phi = 3.50$. The maximum CO selectivities for 1-butanol, 2-butanol, and isobutanol reactions were 69.8, 68.1, and 72.7, respectively. Then the CO selectivity started to fall for $\phi > 3.50$.

3.5 CO₂ Selectivity

As shown in figure 6, the CO₂ selectivity for the reaction of each butanol isomer in the absence of Rh was <20%. In the presence of Rh, the CO₂ selectivity was 100% for the reaction of each butanol isomer at $\phi \leq 0.939$. As the equivalence ratio further increased, the CO₂ selectivity dropped gradually.

3.6 Paraffins Selectivity

Figure 7 illustrates the paraffins selectivity. It was found that paraffins were formed only with the Rh/alumina catalyst when $\phi \geq 4.75$ for 1-butanol and 2-butanol, as well as $\phi \geq 3.50$ for isobutanol. The only paraffin was methane, and there was no ethane, propane, or butane. It was also observed that propylene was formed at the same time with methane.

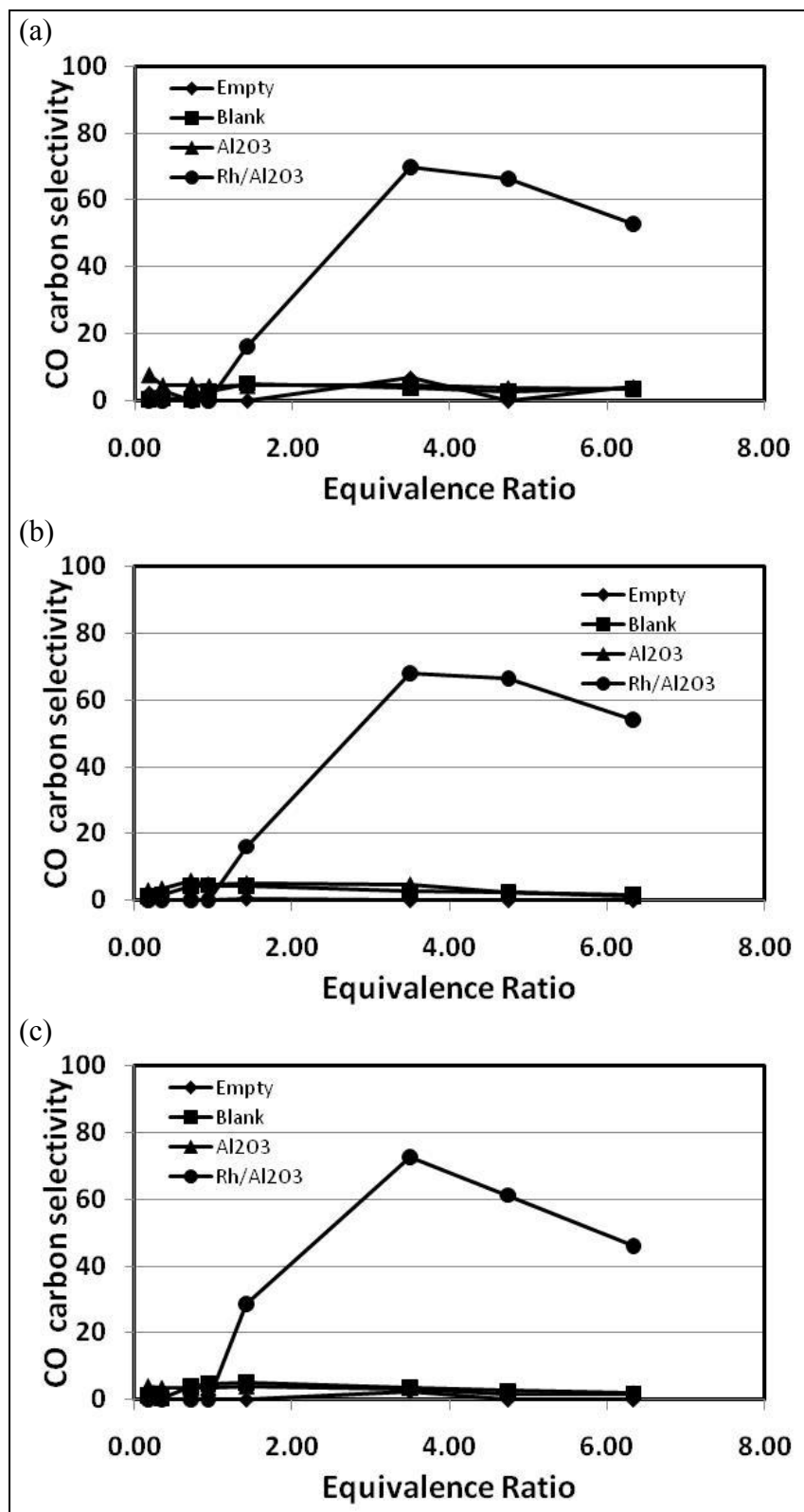


Figure 5. CO selectivity for catalytic oxidative dehydration of butanol isomers with empty tube, blank alumina foam, γ -alumina coated foam, and Rh/alumina foam: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

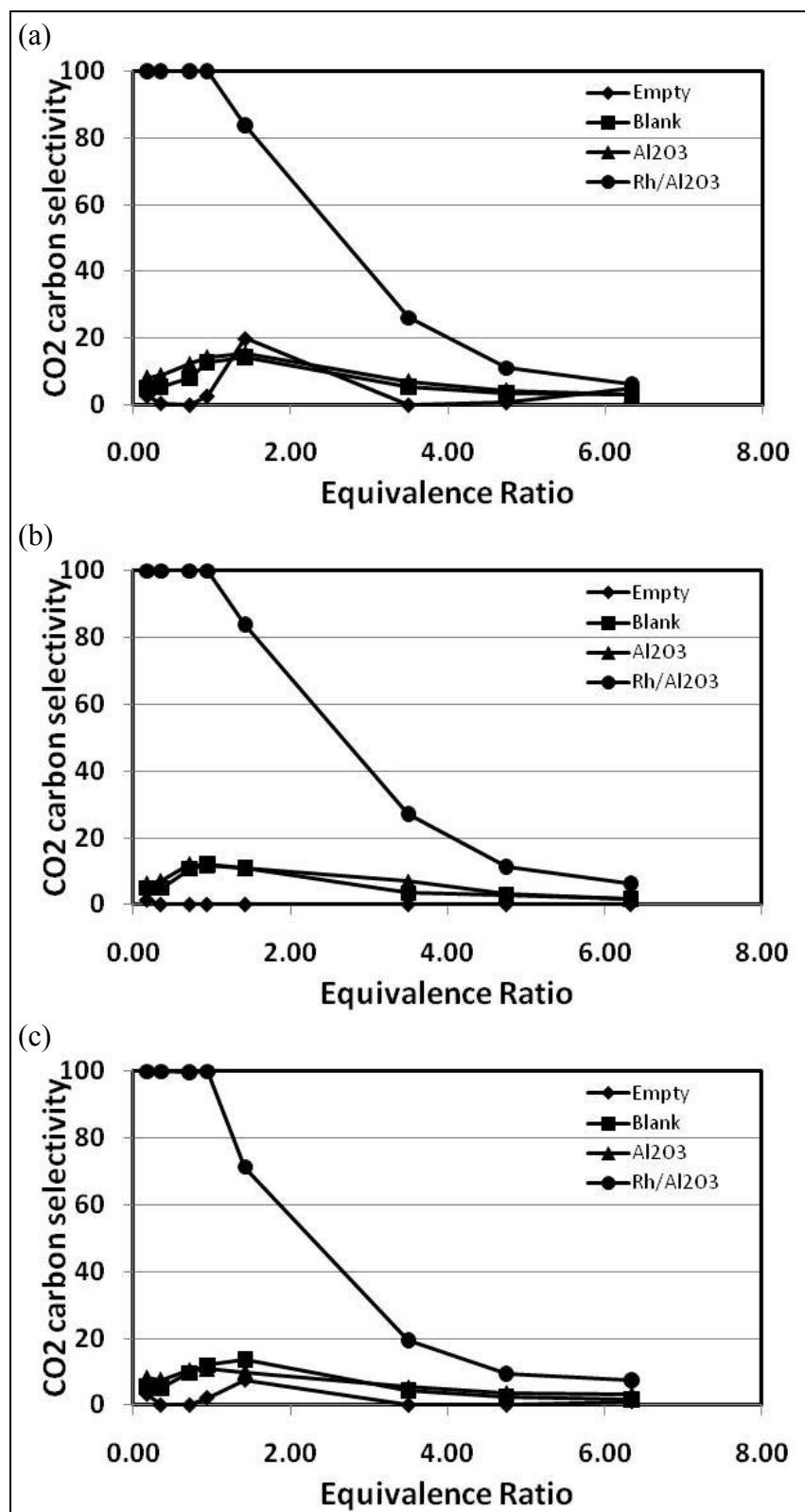


Figure 6. CO₂ selectivity for catalytic oxidative dehydration of butanol isomers with empty tube, blank alumina foam, γ -alumina coated foam, and Rh/alumina foam: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

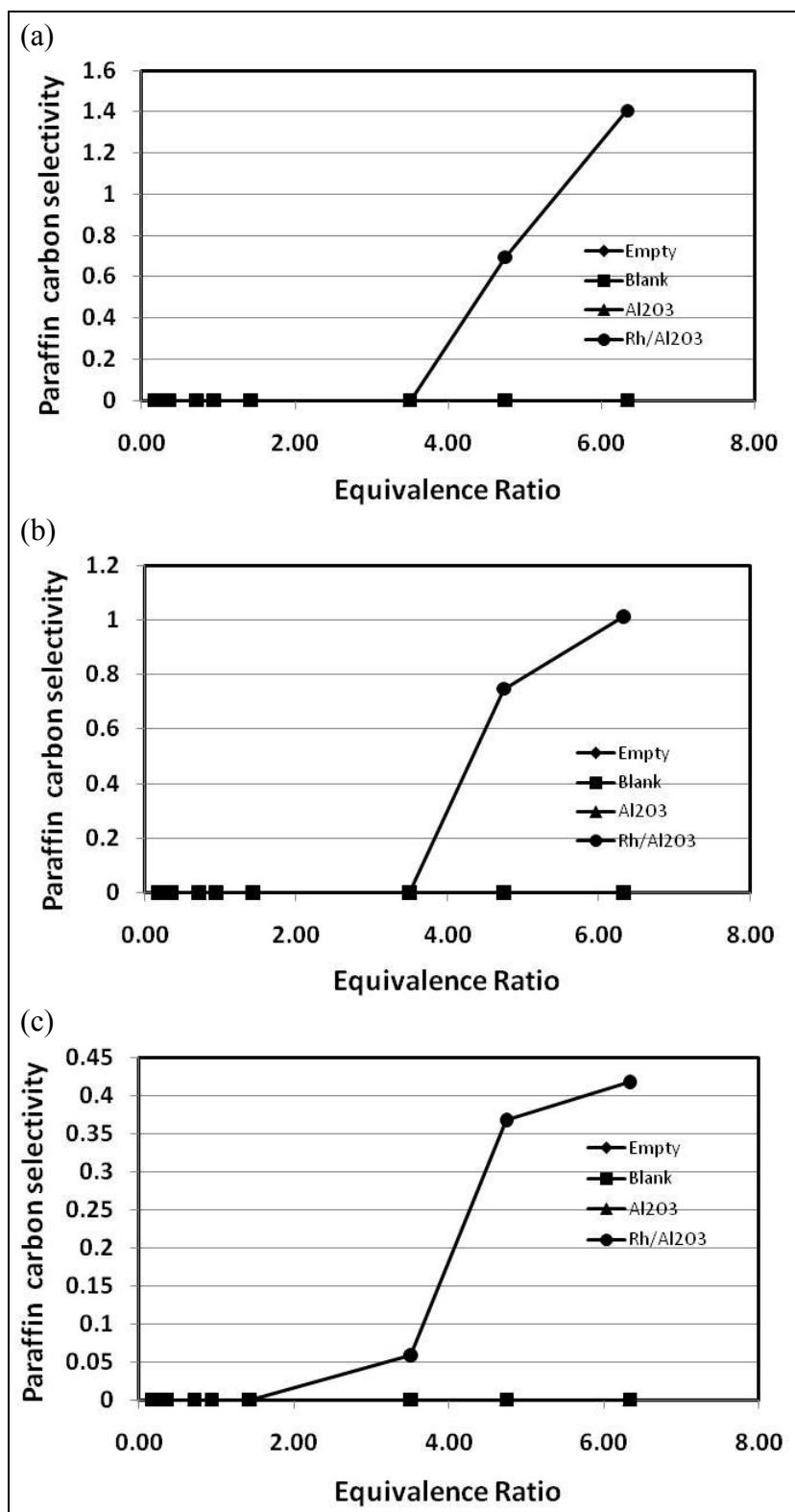


Figure 7. Paraffins selectivity for catalytic oxidative dehydration of butanol isomers with empty tube, blank alumina foam, γ -alumina coated foam, and Rh/alumina foam: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

4. Discussion

4.1 Conversions

By comparing the conversion of the reactor with (1) no foam catalyst, (2) blank alumina foam, (3) γ -alumina coated alumina foam, and (4) the coated alumina foam with Rh added, the relative contributions of various homogeneous and heterogeneous reactions were elucidated. The conversion to known products is low in the empty tube experiments, implying a small contribution from homogeneous reactions at reaction temperatures below 510 °C. In comparison to empty tube experiments, the conversion improved significantly with the presence of a solid phase of alumina or Rh/alumina. The improvement of conversion by the presence of the blank alumina foam indicates surface reactions dominate in the conversion of butanol isomers. The contribution of heterogeneous reactions on alumina was further investigated by changing the surface area of the alumina. For instance, the conversion of isobutanol was over 60% in the presence of the blank alumina foam. The isobutanol conversion was further improved to 80% by adding a coating of γ -alumina onto the alumina foam. A similar trend in conversion was observed with 1-butanol conversion. For 2-butanol, the conversion improvement from the γ -alumina coating is minimal, which again suggests that 2-butanol is so reactive that the conversion is not reaction-limited but mass transfer-limited. In general, the conversion increases in the order of empty tube < blank alumina foam < γ -alumina-coated alumina foam < Rh/ γ -alumina foam. This supports the implication that the contribution of homogenous (gas phase) reaction is relatively small compared to heterogeneous (surface) reactions.

4.2 Dehydration vs. Dehydrogenation

In the absence of Rh in the catalyst, four-carbon olefins were the major products at all equivalence ratios for all three isomers (figure 4). Since a minimal amount of H₂ gas was detected, it implied that dehydration (equation 4) of butanol isomers occurred with negligible dehydrogenation (equation 5) in the empty tube, over the blank alumina foam and γ -alumina foam.



This finding is consistent with a previous study (21), which showed that dehydration is dominant over the dehydrogenation at a higher temperature (>250 °C).

In the presence of Rh, the olefins' selectivity remained <1% for $\phi < 2.0$, which indicates that either there was an alternative pathway other than equations 4 or 5, or the olefins formed through equation 4 were too reactive in the presence of Rh. The olefins' selectivity increased with higher

equivalence ratios. Since the olefins' selectivity depended on O₂ content, the oxidation of olefins could be the reason why the selectivity was negligible at $\phi < 2.0$ and increases for $\phi > 2.0$.

4.3 Olefins Distribution

In this study, it was assumed that the reaction underwent unimolecular elimination (E1) mechanism; therefore, carbocation was the intermediate of the reaction. According to Macho et al., dehydration of C₄ alcohol would produce a corresponding carbocation intermediate, followed by isomerization of this carbocation producing olefins (figure 8) (19). In this section, the focus is on the olefin distribution using the γ -alumina-coated foam and the Rh/Al₂O₃ catalyst. The olefin distribution using the empty tube and the blank foam can be found in the supplemental materials. First, the degree of C-C bond scission was determined by analyzing the butenes/(total olefins) ratio (table 1 in Supplemental Materials). The degree of skeletal isomerization of the carbocations could be indicated by the 1-butene/2-butene ratio (table 2 in Supplemental Materials) and the isobutene/(linear butene ratio) (table 4 in Supplemental Materials). In addition, the cis/trans ratio would provide information on the surface geometric effect (table 3 in Supplemental Materials).

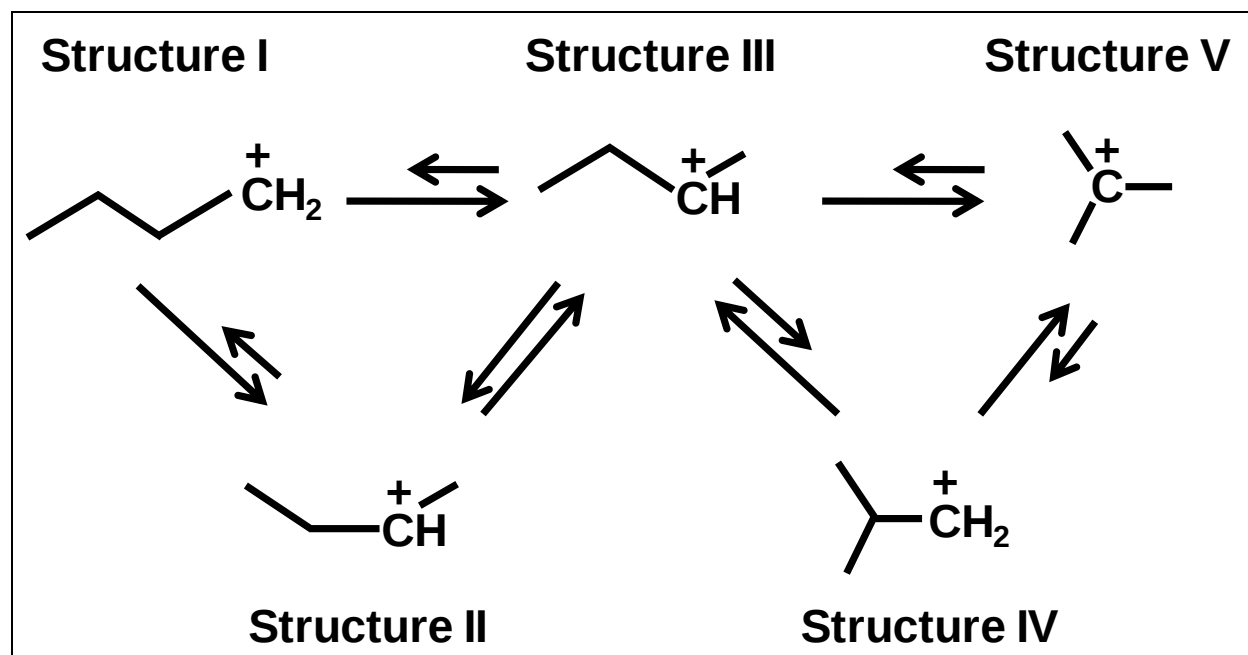


Figure 8. Isomerization of Carbocations from the dehydration of C₄ alcohols (19).

In catalytic oxidative dehydration of 1-butanol, the primary carbocation (Structure I in figure 8) was formed initially. There was minimal thermal cracking along the carbon backbone since 88–99% of the olefins produced were butene isomers. Then the degree of isomerization of the initially formed carbocation was determined by 1-butene/2-butenes ratio (A/B) and isobutene/(linear butenes) ratio. It was found that the isomerization from primary carbocation

(Structure I) to secondary carbocation (Structure II or III) was between 42% and 28%, depending on the catalyst configuration and equivalence ratio (equation 6):

$$PS = 1/(1+A/B), \quad (6)$$

where PS represents the degree of isomerization from primary to secondary carbocation, and A/B represents the 1-butene/2-butenes ratio. The 1-butene/2-butenes ratio was determined to be between 1.4 and 2.6. Although trans-2-butene was generally believed to be more stable than cis-2-butene in gas phase reaction due to steric hindrance, cis carbocation was found to be the preferred surface orientation, as indicated by cis/trans ratio greater than 1. Since the isobutene/(linear butenes) ratio was zero, there was no isomerization to tertiary carbocation (Structure V).

Similarly, secondary carbocation (Structure II or III) was formed initially during catalytic oxidative dehydration of 2-butanol. Like 1-butanol, there was minimal thermal cracking of the hydrocarbon backbone since the typical butenes/(total olefin) ratio was 0.98-0.99. It was found that about 33–37% of the secondary carbocation isomerized to form the primary carbocation (equation 7):

$$SP = (A/B) / (1+A/B), \quad (7)$$

where SP represents the degree of isomerization from secondary carbocation to primary carbocation. The 1-butene/2-butenes ratio (A/B) was between 0.49 and 0.59, depending on the catalyst configuration and equivalence ratio. Again, the cis-carbocation was the preferred surface orientation over the trans-carbocation. Since the isobutene/linear butenes ratio was zero, there was no isomerization to tertiary carbocation.

Finally, the branched carbocation intermediate (Structure IV) from catalytic oxidative dehydration of isobutanol isomerizes to all other four carbocation structures. There was minimal thermal cracking since the butenes/(total olefins) ratio was between 0.98 and 0.99. About 74–80% of branched carbocation (Structure IV) isomerized to tertiary carbocation (Structure V) according to equation 8:

$$BT = (i/L)/(1+i/L), \quad (8)$$

where i/L represents isobutene/(linear butenes) ratio with typical values of 2.9-3.9, depending on the catalyst configuration and equivalence ratio. The remaining 20–26% of branched carbocation isomerized to form secondary carbocation. Since the cis/trans ratio was greater than 1 with alumina-coated foam, the cis-carbocation was the preferred orientation. In contrast, the trans-carbocation was preferred on Rh/alumina catalyst. Moreover, the typical 1-butene/2-butene ratio was 0.73-0.92. According to equation 7, about 42–48% of the secondary carbocations (Structure III and III) isomerized to primary carbocation (Structure I).

4.4 Oxidation Over Rh/Al₂O₃

The CO selectivity provided an evidence for the oxidation of olefins over the Rh. The empty tube, blank alumina foam, and the γ -alumina-coated foam produced a negligible amount of CO (<10% selectivity) at all equivalence ratios for all three butanol isomers. However, partial oxidation of olefins occurred over the Rh/alumina catalyst for $\phi > 0.94$.



The CO₂ selectivity confirmed that oxidation reaction occurred. In the experiments with an empty tube, blank alumina, and the γ -alumina-coated foam, CO₂ selectivity of each butanol isomer reached a maximum of about 15% at $\phi = 1.42$. This indicates that there were some combustion activities in the gas phase. In contrast, the CO₂ selectivity of each butanol isomer over Rh/alumina catalyst was 100% for $\phi \leq 0.94$. This suggested that the C₄H₈ from dehydration (equation 4) was fully oxidized at high enough O₂ concentration through equations 9 and 10.



When $\phi > 0.94$, there was not enough O₂ to fully combust the olefins. Therefore, CO₂ selectivity dropped gradually with a gradual increase in CO selectivity. When $\phi > 3.50$, there was not enough O₂ to partial oxidize the olefins. Therefore, CO selectivity dropped gradually and olefins selectivity increased simultaneously.

4.5 Cracking Reactions

In absence of Rh, no paraffin was formed. However, a small amount of all isomers was cracked to produce a C3 fragment and a C1 fragment in the presence of Rh at $\phi > 3.5$. The absence of C5 fragment (pentane or pentenes) indicated that there was no cracking from a C8 dimer intermediate. The C3 fragment was propylene, not propane. No ethane was observed, but methane was formed. Since the carbon selectivity of propylene was approximately three times than that of methane, the following cracking reaction may occur on an H-covered Rh surface to produce both propylene and methane when O₂ is limited:



In contrast, equilibrium calculations have shown that the cracking reactions of butanol produced only methane at high ϕ (>1.4), which is different from our experimental results. This can be explained by the effect of contact time. Our results were obtained at contact time of 25 ms, which could be too short to achieve equilibrium composition. This explanation is consistent with the study on isobutanol conversion with different contact times (22), in which the propylene selectivity increased from 4.4% to 14.3%, as the contact time increased from 25 ms to 125 ms. This demonstrates that C-C bond scission is favored with a longer contact time. As also shown in equilibrium calculations, all C-C bonds would have been broken to form CO, CO₂, and methane at equilibrium (i.e., contact time approaches infinity).

4.6 Proposed Reaction Mechanism

From this study, a mechanism of catalytic oxidative dehydration of butanol is proposed in figure 9. The majority of butanol reacts to produce olefins on the alumina surface, which involves C-O bond scission. At the same time, the contribution of gas phase reaction is smaller. Isomerization of the carbocations results in a mixture of butene isomers. Then the olefins are oxidized on the Rh in the presence of O_2 to produce CO and/or CO_2 , depending on the availability of O_2 . Adsorption geometry of the surface species will be the subject of future studies.

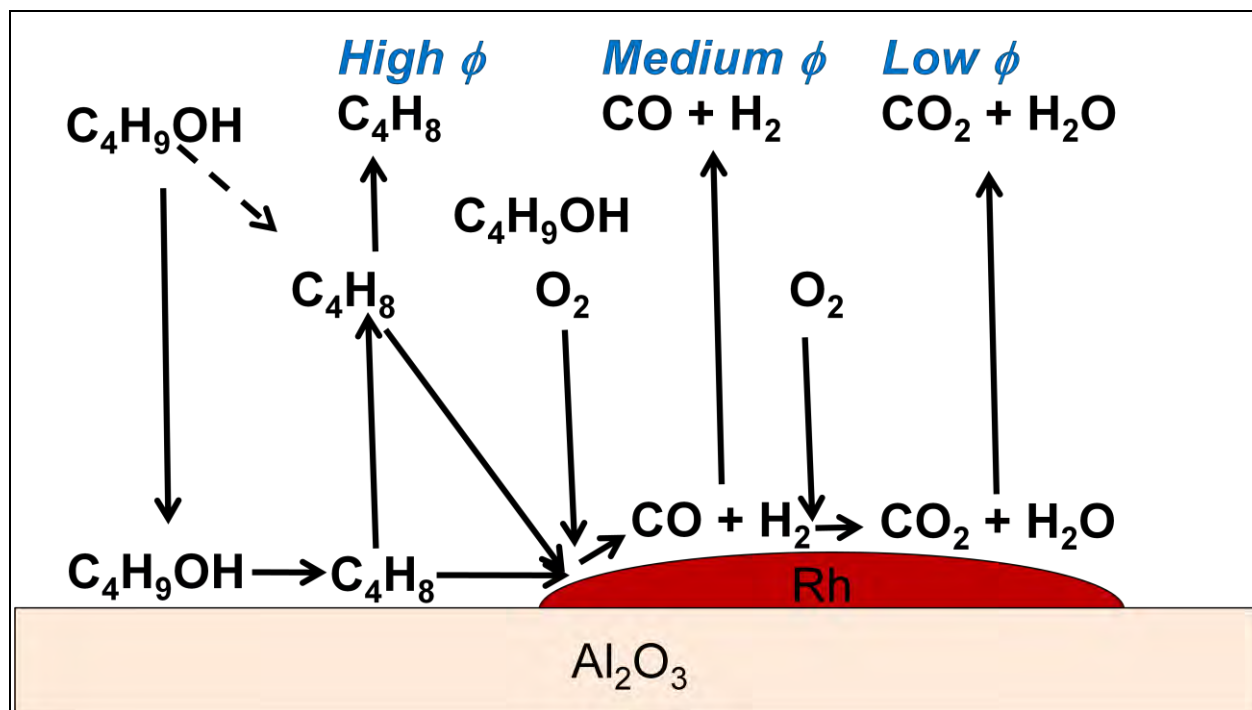


Figure 9. Proposed mechanism for the catalytic oxidative dehydration of butanol isomers.

5. Conclusions

Catalytic oxidative dehydration of 1-butanol, 2-butanol, and isobutanol was investigated with short contact time (25 ms). Product selectivity was compared with several configurations including empty tube, blank alumina foam, γ -alumina-coated foam, and addition of Rh. It was found that the majority of butanol dehydrates to form four-carbon olefinic species on the alumina surface. Depending on the availability of O_2 , these olefins were further oxidized to form CO and/or CO_2 .

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Supplemental Materials

Table 1. Butenes/(Total Olefins) Ratio for reactions of butanol isomers: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

(a)

ϕ	Empty	Blank	Al ₂ O ₃	Rh/Al ₂ O ₃
0.1757	0.6613	0.9908	0.9823	No Olefins
0.3502	0.5236	1.000	0.9812	No Olefins
0.7189	0.5202	1.000	0.9811	No Olefins
0.9392	0.5442	0.9915	0.9827	No Olefins
1.4252	0.7159	0.9829	0.9793	No Olefins
3.5018	0.6900	0.9788	0.9778	0.7593
4.7450	0.5778	0.9753	0.9801	0.8740
6.3383	0.5771	0.9704	0.9532	0.8737

(b)

ϕ	Empty	Blank	Al ₂ O ₃	Rh/Al ₂ O ₃
0.1757	0.9643	0.9889	0.9832	No Olefins
0.3501	0.9971	0.9872	0.9841	No Olefins
0.7187	1.000	0.9900	0.9864	No Olefins
0.9390	1.000	0.9917	0.9885	No Olefins
1.4248	1.000	0.9933	0.9889	No Olefins
3.5010	1.000	0.9915	0.9987	1.000
4.7484	1.000	0.9924	0.9952	0.9884
6.3312	0.9830	0.9916	0.9937	0.9789

(c)

ϕ	Empty	Blank	Al ₂ O ₃	Rh/Al ₂ O ₃
0.1757	0.8988	0.9727	0.9680	No Olefins
0.3501	0.9179	0.9252	0.9743	No Olefins
0.7187	0.9297	0.9097	0.9803	No Olefins
0.9390	0.9305	0.9234	0.9812	No Olefins
1.4248	0.9308	0.9260	0.9823	No Olefins
3.5010	0.9263	0.9173	0.9861	0.8760
4.7464	0.9203	0.9203	0.9866	0.9347
6.3377	0.9151	0.9318	0.9850	0.9511

Table 2. 1-Butene/2-Butenes Ratio for reactions of butanol isomers: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

(a)

ϕ	Empty	Blank	Al_2O_3	$\text{Rh}/\text{Al}_2\text{O}_3$
0.1757	5.217	1.406	2.026	No Olefins
0.3502	14.83	1.472	2.080	No Olefins
0.7189	Only 1-Butene	1.416	2.157	No Olefins
0.9392	Only 1-Butene	1.429	2.326	No Olefins
1.4252	Only 1-Butene	1.431	2.397	No Olefins
3.5018	Only 1-Butene	1.465	2.451	7.854
4.7450	Only 1-Butene	1.500	2.509	1.774
6.3383	3.989	1.518	2.599	2.167

(b)

ϕ	Empty	Blank	Al_2O_3	$\text{Rh}/\text{Al}_2\text{O}_3$
0.1757	0.6303	0.6053	0.5946	No Olefins
0.3501	0.6304	0.6002	0.5791	No Olefins
0.7187	0.6318	0.5944	0.5914	No Olefins
0.9390	0.6330	0.5927	0.5928	No Olefins
1.4248	0.6323	0.5898	0.5947	No Olefins
3.5010	0.6373	0.5931	0.5866	0.4960
4.7484	0.6388	0.5937	0.5722	0.4867
6.3312	0.6407	0.6047	0.5757	0.5082

(c)

ϕ	Empty	Blank	Al_2O_3	$\text{Rh}/\text{Al}_2\text{O}_3$
0.1757	1.798	0.9323	0.9101	No Olefins
0.3501	1.922	0.9252	0.9131	No Olefins
0.7187	1.916	0.9097	0.9053	No Olefins
0.9390	1.911	0.9234	0.9138	No Olefins
1.4248	1.879	0.9260	0.9155	No Olefins
3.5010	1.883	0.9173	0.9118	Only 1-butene
4.7464	1.929	0.9203	0.8948	0.7337
6.3377	1.125	0.9318	0.8737	0.8391

Table 3. Cis/Trans Ratio for reactions of butanol isomers: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

(a)

ϕ	Empty	Blank	Al ₂ O ₃	Rh/Al ₂ O ₃
0.1757	Only trans-2-butene	1.183	1.330	No Olefins
0.3502	Only trans-2-butene	1.208	1.355	No Olefins
0.7189	No 2-butenes	1.192	1.366	No Olefins
0.9392	No 2-butenes	1.202	1.392	No Olefins
1.4252	No 2-butenes	1.199	1.404	No Olefins
3.5018	No 2-butenes	1.196	1.364	Only trans-2-butene
4.7450	No 2-butenes	1.204	1.353	1.104
6.3383	Only trans-2-butene	1.213	1.331	1.160

(b)

ϕ	Empty	Blank	Al ₂ O ₃	Rh/Al ₂ O ₃
0.1757	1.035	1.145	1.184	No Olefins
0.3501	1.034	1.143	1.207	No Olefins
0.7187	1.031	1.151	1.171	No Olefins
0.9390	1.032	1.152	1.205	No Olefins
1.4248	1.030	1.149	1.207	No Olefins
3.5010	1.026	1.154	1.241	0.8862
4.7484	1.025	1.175	1.357	1.089
6.3312	1.024	1.171	1.414	1.110

(c)

cis/trans Ratio	Empty	Blank	Al ₂ O ₃	Rh/Al ₂ O ₃
0.1757	0.107	1.057	1.355	No Olefins
0.3501	No cis-2-butene	1.068	1.364	No Olefins
0.7187	No cis-2-butene	1.056	1.387	No Olefins
0.9390	No cis-2-butene	1.056	1.377	No Olefins
1.4248	No cis-2-butene	1.061	1.351	No Olefins
3.5010	No cis-2-butene	1.078	1.291	No 2-butenes
4.7464	No cis-2-butene	1.060	1.471	0.7337
6.3377	0.738	1.078	1.580	0.8391

Table 4. Isobutene/(Linear Butenes) Ratio for reactions of butanol isomers: (a) 1-butanol, (b) 2-butanol, and (c) isobutanol.

(a)

ϕ	Empty	Blank	Al_2O_3	$\text{Rh}/\text{Al}_2\text{O}_3$
0.1757	0	0	0	No Olefins
0.3502	0	0	0	No Olefins
0.7189	0	0	0	No Olefins
0.9392	0	0	0	No Olefins
1.4252	0	0	0	No Olefins
3.5018	0	0	0	0
4.7450	0	0	0	0
6.3383	0	0	0	0

(b)

ϕ	Empty	Blank	Al_2O_3	$\text{Rh}/\text{Al}_2\text{O}_3$
0.1757	0	0	0.02096	No Olefins
0.3501	0	0	0.01019	No Olefins
0.7187	0	0	0	No Olefins
0.9390	0	0	0	No Olefins
1.4248	0	0	0	No Olefins
3.5010	0	0	0	0
4.7484	0	0	0	0
6.3312	0	0	0	0

(c)

ϕ	Empty	Blank	Al_2O_3	$\text{Rh}/\text{Al}_2\text{O}_3$
0.1757	2.432	1.753	3.195	No Olefins
0.3501	2.501	1.794	3.223	No Olefins
0.7187	2.481	1.873	3.362	No Olefins
0.9390	2.504	1.920	3.394	No Olefins
1.4248	2.504	1.913	3.316	No Olefins
3.5010	2.505	1.938	3.140	18.81
4.7464	2.532	1.913	3.509	2.928
6.3377	2.060	1.921	3.866	2.953

List of Symbols, Abbreviations, and Acronyms

CO	carbon monoxide
CO ₂	carbon dioxide
GC	gas chromatograph
HP-INNOWAX	Brand name of a separation column for gas chromatography
HPLC	High Performance Liquid Chromatography
MTBE	methyl tert-butyl ether
N ₂	nitrogen
O ₂	oxygen

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