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# Autothermal partial oxidation of butanol isomers

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# ABSTRACT

The four isomers of butanol offer an interesting platform from which to study the reaction pathways of alcohols in an autothermal partial oxidation system, as they comprise one tertiary, one secondary, and two primary alcohols with the same number of carbon atoms. We demonstrate high yields of syngas or unsaturated molecules at contact times on the order of 10 ms, and investigate the reaction pathways of each isomer over Rh, RhCe, Pt, and PtCe catalysts for a range of carbon-to-oxygen (C/O) ratios.

For each isomer, conversion to equilibrium syngas products is essentially complete at C/O = 0.8. As C/O ratio increases, the major product from the primary and secondary butanols switches to the corresponding carbonyl, producing butyraldehyde, isobutyraldehyde, and butanone from 1-butanol, isobutanol and 2-butanol, respectively. Selectivity to the carbonyls approached 30–50% as C/O approached 2.0. Dehydration to the corresponding butenes is relatively minor in comparison, representing less than 20% selectivity at C/O = 2.0. tert-butanol reacted differently, selecting mainly for the dehydration product isobutene. Acetone was the main carbonyl product from *tert*-Butanol, but selectivity to acetone was always  $\leq$  10%. Global mechanisms in an autothermal reactor, based on pyrolysis, combustion and surface science literature, are proposed for each alcohol. Surface chemistry likely accounts for much of the syngas formation and heat generation, while the carbonyls and alkenes may be formed primarily through homogeneous routes. © 2011 Elsevier B.V. All rights reserved.

# 1. Introduction

Significant research effort in recent years has focused on the development of renewable liquid fuels in order to decrease the economic and environmental impacts of fossil fuel consumption. Four-carbon alcohols have received particular attention because they can be produced in significant quantities from a variety of renewable feedstocks [1-7] and have several advantages over short-chain alcohols. In particular, the butanols have many properties similar to currently consumed fossil fuels, including high energy density, low hygroscopicity, and low corrosivity [8,9].

Autothermal partial oxidation over noble metal catalysts has shown promise as a technique to convert a variety of feedstocks (both renewable and fossil fuel-based) into syngas (a mixture of H<sub>2</sub> and CO) and longer-chain unsaturated molecules, both of which are important intermediates in the synthesis of a wide range of molecules [10-16]. Additionally, these reactions are carried out at high temperatures with heat generated in situ and occur on millisecond time scales, allowing for the use of small and

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simple reactors that are appropriate for utilizing diffuse renewable resources

Recently, St. Clair and Lee [17] studied the autothermal partial oxidation of isobutanol over Rh and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and found that Rh gave high yields of syngas while  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> selected primarily for the dehydration product isobutene. We have recently shown that the addition of Ce to Rh catalysts improves yields of hydrogen from several fuels [10,11,15,18], and that autothermal short contact time (SCT) reactors can also give high yields to nonequilibrium products from light oxygenates [16,19]. Additionally, we proposed that the behavior of a model compound of different functional group classes (e.g. C<sub>2</sub> alcohols, aldehydes, and acids) in an autothermal SCT reactor could be extrapolated to other molecules in the same class [16].

In this work we apply autothermal partial oxidation of the four butanol isomers over Rh, RhCe, Pt, and PtCe catalysts to show that, depending upon operation parameters, high selectivity to syngas or nonequilibrium products may be obtained. We note that although the formation of the nonequilibrium products may be primarily homogeneous, the exothermic reactions that occur mainly on the catalyst surface are required to provide heat for gas-phase dehydrogenation and dehydration reactions. Additionally, the behavior of the primary butanols during autothermal processing appears to be similar to ethanol [16], supporting the hypothesis that members of a functional group family behave similarly in autothermal SCT reactors.

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#### 2. Experimental

Experiments were carried out with a 19 mm ID quartz tube as shown in Fig. 1. Liquid fuel was fed through a stainless steel nebulizer at the top of the reactor at 1 mLmin<sup>-1</sup> and was atomized with 0.7 SLPM  $N_2$ . Remaining  $N_2$  and  $O_2$  were fed around the nebulizer, and total N<sub>2</sub> and O<sub>2</sub> were maintained at air stoichiometry. Gas flow rates were varied to obtain different carbon-to-oxygen (C/O)ratios. defined as the molar ratio of carbon in the feed molecule to atomic oxygen in the O<sub>2</sub> feed. The catalyst bed was positioned 30 cm below the nebulizer and reactor walls between the nebulizer and catalyst were maintained at 175 °C to vaporize the fuel. An 80 pores-per-linear-inch (ppi)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> foam monolith (Südchemie) was positioned 3.5 cm upstream of the catalyst bed to mix reactants. The catalyst bed was comprised of 3.25 g of 1.3 mm catalytic spheres. The spheres (St. Gobain-Norpro) consisted of 1 wt% M or 1 wt% M-1 wt% Ce supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, where M = Rh or Pt. A 65 ppi  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> foam monolith served as a back heat shield and to hold thermocouples in place. Type K thermocouples (Omega) were located at the upstream and downstream edges of the sphere bed, and the entire bed was wrapped with aluminosilicate cloth insulation to prevent heat loss and gas bypass during the experiment. Spheres were prepared by incipient wetness impregnation of aqueous catalyst precursor salts ( $Rh(NO_3)_3$ ,  $H_2PtCl_6$ , and  $Ce(NO_3)_3$ ) followed by drying under vacuum. Rh and RhCe catalysts were produced in multiple cycles of deposition-dry-calcination at 600 °C, where the calcination duration was ten minutes (to decompose the nitrate salt), followed by a final calcination at 600 °C for 6 h. Pt and



Fig. 1. Reactor configuration for the autothermal partial oxidation of the butanol isomers.



**Fig. 2.** Conversion and catalyst backface temperature of the four butanol isomers for each catalyst as a function of C/O ratio. (a) 1-Butanol, (b) isobutanol, (c) 2-butanol and (d) *t*-butanol.



Fig. 3. Selectivities to H<sub>2</sub> and H<sub>2</sub>O from each isomer as a function of C/O ratio over all four catalysts. (a) 1-Butanol, (b) isobutanol, (c) 2-butanol and (d) t-butanol.

PtCe catalysts were prepared without the brief calcination steps and were reduced under flowing  $H_2$  and  $N_2$  at 600 °C for 6 h. The multistep calcination procedure was adopted for the Rh-based catalysts to avoid loss of catalyst metal through delaminating bubbles that formed when a concentrated precursor solution was used. For the Pt-based catalysts, the reduction procedure was employed to mitigate metal loss through volatile intermediates in the decomposition of the precursor salt.

Analysis of products was performed on an HP6890 gas chromatograph equipped with thermal conductivity (TCD) and flame ionization detectors (FID). The column was 30 m with a PLOT-Q stationary phase. N<sub>2</sub> from the feed was used as an internal standard. H<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub> were quantified with the TCD, while all others were quantified with the FID, except H<sub>2</sub>O, which was calculated by difference from an oxygen atom balance. Carbon and hydrogen atom balances typically closed within 10%. Each data point shown represents the average of three runs, and 95% confidence intervals were generally 5–10% absolute. Products up to C<sub>6</sub> were analyzed, but no products > C<sub>4</sub> were detected in selectivity >1%. Each catalyst was run for at least 12 h without any observable deactivation.

# 3. Results

### 3.1. Conversion and temperature

Each of the butanols sustained autothermal operation for  $0.8 \le C/O \le 2.0$ , and higher C/O ratios were not attempted. At C/O = 0.8, conversion was  $\ge 99\%$  and selectivities closely reflect those predicted by thermodynamic equilibrium, which is primarily syngas.

Conversion and back face temperature data are shown in Fig. 2. At the temperatures observed here, residence times ranged from 6 to 20 ms, calculated at the temperatures reported in Fig. 2.

Conversion was similar for 1-butanol across all four catalysts and was essentially complete at  $C/O \le 1.0$ , as shown in Fig. 2. The Pt catalysts yielded a higher temperature at the downstream edge of the catalyst bed than their Rh counterparts by 50-100 °C. 2-Butanol was similar to 1-butanol in that conversion was generally similar across catalysts, and temperatures were higher over Pt-based than Rh-based catalysts. Conversion of tert-butanol was generally higher than the other butanols (Fig. 2), possibly due to its greater tendency toward homogeneous pyrolysis. Like 1-butanol and 2-butanol, the Pt catalysts gave a higher back face temperature that corresponded to a lower selectivity to CO and H<sub>2</sub> (Fig. 3). Conversion of isobutanol fell off faster than the other isomers as C/O ratio increased (Fig. 2). For isobutanol, the Pt catalyst operated roughly 100°C higher than PtCe over the entire C/O range; for the other three isomers, PtCe gave temperatures comparable to or higher than the Pt catalyst.

# 3.2. Syngas and combustion products

At C/O  $\leq$  1.2, CO and H<sub>2</sub> were favored from all four isomers, as shown in Figs. 3 and 4. Rh and RhCe generally gave higher conversion to syngas than the Pt catalysts, and PtCe gave significantly lower syngas yields than the other three catalysts for C/O  $\geq$  1.4. The lower selectivity to syngas from the Pt-based catalysts is consistent with the lower steam reforming activity of Pt [20,21], although the selectivity to H<sub>2</sub>O was not significantly higher.



**Fig. 4.** Selectivities to CO and CO<sub>2</sub> from each isomer as a function of C/O ratio over all four catalysts. 'Other' represents the sum of all carbonaceous products other than CO and CO<sub>2</sub>. For clarity, only the minimum and maximum lines are shown. (a) 1-Butanol, (b) isobutanol, (c) 2-butanol and (d) *t*-butanol.

 $H_2O$  and  $CO_2$  were present at 20–30% selectivity regardless of catalyst or isomer;  $H_2O$  was present in slightly higher selectivity over the PtCe catalyst, although the magnitude of difference is near the limit of experimental uncertainty.

#### 3.3. C<sub>4</sub> intermediates

1-Butanol, 2-butanol and isobutanol gave high selectivity to carbonyl products as C/O ratio increased, with relatively minor selectivity to  $C_4$  olefins as shown in Fig. 5. The trend for *tert*-butanol was reversed, with isobutene as the major product.

From the primary butanols, selectivity to the aldehyde reached 20–30% as C/O approached 2.0, though the Rh catalyst showed lower selectivity to isobutyraldehyde. Selectivity to butanone from 2-butanol reached 35–45% for the same C/O range. For 1-butanol over all catalysts and for 2-butanol over the Pt-based catalysts, selectivity to the carbonyl at C/O  $\leq$  1.4 was comparable to butene selectivity (shown as a sum of 1-butene and both 2-butene isomers), but at C/O = 2.0, the carbonyl was favored by a factor of 2–3. The ratio of carbonyl to butene was even higher over the Rh catalysts for 2-butanol, reaching a factor of 5–10 in preference of the carbonyl. For isobutanol, selectivity at C/O = 2.0 favored the carbonyl over isobutene by a factor of 3–5.

Because *tert*-butanol lacks an  $\alpha$ -H atom, formation of a carbonyl cannot occur through simple hydrogen abstraction reactions. A dehydration route to isobutene is thus predominant, with selectivities to isobutene reaching 60–70% over the Pt catalysts and 30–50% over the Rh catalysts. Acetone was the main carbonyl

product formed from *tert*-butanol, but represented  $\leq$ 10% selectivity at all C/O ratios investigated.

### 3.4. Other intermediates

The other species observed in significant amounts were generally only ethylene and propylene. Selectivities to these two olefins were similar over 1-butanol at 5–15% for C/O  $\ge$  1.4, regardless of catalyst. Isobutanol, however, showed higher selectivity to propylene at 10–20% for  $C/O \ge 1.4$  and only minor selectivity to ethylene, at  $\leq$ 5%. The difference in selectivity to propylene from isobutanol across catalysts cannot be explained by temperature alone. Pt and Rh, which displayed the highest and lowest backface temperatures, respectively (Pt was over 100 °C higher than Rh at all C/O ratios), gave comparable selectivities to propylene, while RhCe and PtCe give noticeably higher selectivity to propylene. This observation suggests that either production or consumption of propylene (or both) occurs to some extent on the catalyst surface. 2-butanol and tert-butanol showed lower selectivities to these two olefins, although 2-butanol produced significant selectivity to each over PtCe. It is difficult to discern the role of the PtCe catalyst in the formation of ethylene and propylene from 2-butanol because the range over which their selectivities are significant corresponds to the range where PtCe temperature was nearly 100 °C higher than the other catalysts. Their formation may therefore be homogeneous, possibly from the thermal decomposition of 1- and 2-butenes, which is discussed below (Fig. 6).



**Fig. 5.** Selectivities to major carbonyl and C<sub>4</sub> olefins from each isomer as a function of C/O ratio over all four catalysts. Butenes represents the sum of butene isomers. (a) 1-Butanol, (b) isobutanol, (c) 2-butanol and (d) *t*-butanol.

# 4. Discussion

#### 4.1. Chemistry of the isomers

Reaction schemes within a CPO reactor are complex networks of homogeneous and heterogeneous reactions that are difficult to untangle from analysis of integral data. However, the reaction schemes shown below are not unprecedented in the literature, and by observation of reaction intermediates and comparison between catalysts, a qualitative formulation of the dominant reaction pathways is possible.

#### 4.1.1. 1-Butanol

Alcohols generally decompose by either dehydrogenation to produce a carbonyl or dehydration to produce an alkene [22,23]. For 1-butanol, dehydration and dehydrogenation routes are competitive in the gas phase in the absence of  $O_2$  up to 500 °C, while dehydrogenation predominates at higher temperatures [22,24]. This scheme is consistent with the product spectrum observed here, as temperatures were well above 500 °C and selectivity to the primary products at high C/O ratios (where secondary reactions are less favored) demonstrates 2–3-fold difference in selectivity in favor of the aldehyde over the alkenes. As C/O decreases (and temperature increases), these primary products can further decompose. The butyraldehyde intermediate can react by decarbonylation to yield CO, H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>, or by demethylation to yield propanal and a CH<sub>x</sub> radical; the butenes may decompose to produce propylene and a CH<sub>x</sub> radical [22,24,25]. Ethylene may be formed by reactions

of several intermediate species via demethylation and dehydration reactions [24,26].

Other than the lower selectivity to syngas species for PtCe, there are few features in the selectivity data to aid in distinguishing between the different catalyst surfaces for 1-butanol. Further discussion of potential surface reactions of 1-butanol will therefore not be attempted here; potential surface mechanisms of alcohols in general are discussed below.

# 4.1.2. 2-Butanol

The major non-equilibrium product from 2-but anol for C/O > 1.2was butanone, which reached 35-45% selectivity as C/O increased to 2.0. At C/O < 1.4 over the Pt catalysts, dehydration reactions appeared to be competitive with dehydrogenation, as selectivities to the butenes and butanone were comparable. When the butenes were produced in  $\geq 2\%$  selectivity, 1-butene was favored over either isomer of 2-butene, with selectivities to 1-butene, cis-2-butene, and trans-2-butene present generally in the ratio 2:1:1, respectively. Negligible selectivity to acetaldehyde (<1%) and only minor selectivity to propanal were observed in these experiments over any of the catalysts, despite their prominence in the 2-butanol pyrolysis literature [22,27]. We note here that  $O_2$  conversion was less than 100% under some reaction conditions (PtCe for  $C/O \ge 1.2$ ); in other similar experiments, the presence of O<sub>2</sub> significantly decreased selectivity to acetaldehyde [16,28], and in 2-butanol combustion, acetaldehyde and propanal were much less prominent [29]. These observations likely mean that oxygen persists until near the downstream edge of the catalyst bed, at least for the PtCe catalyst. This



Fig. 6. Selectivities to ethylene and propylene as a function of C/O ratio over all four catalysts. (a) 1-Butanol, (b) isobutanol, (c) 2-butanol and (d) t-butanol.

hypothesis is also consistent with the very small amounts of hydrocarbon products observed both here and in 2-butanol combustion [29].

PtCe showed a higher selectivity to the ethylene and propylene than the other three catalysts, despite the observed  $O_2$  breakthrough. As discussed above, the range of C/O ratios over which these two alkenes show significant selectivity corresponds to significantly higher temperatures over PtCe; we thus surmise that they may be produced by homogeneous decomposition of either butanone (via unstable ketene intermediates [30]) or the butenes [25,31]. Indeed, CH<sub>4</sub> (not shown) was produced in nearly equal quantities as  $C_3H_6$ , which is expected from the pyrolysis of 1- and 2-butene; the additional  $C_2H_4$  may have been produced by oxidative [23] or nonoxidative [30] decomposition of butanone. CH<sub>4</sub> can also be produced by pyrolysis of butanone by reactions that also produce acetone and propanal [22], but the negligible selectivity to acetone and propanal suggests that these pathways are minor.

#### 4.2. tert-Butanol

Other than the four equilibrium species, *tert*-butanol yielded only one main product, isobutene, which approached 70% selectivity over PtCe at C/O=2.0. Other light olefins were never present in  $\geq$ 1% selectivity, and acetone, the primary carbonyl-containing product, was always  $\leq$  10% selectivity. Over PtCe, selectivity to propanal (not shown) was comparable to acetone.

Isobutene may result mainly from homogenous dehydration, either molecularly or through sequential H and OH radical abstractions [26]. It is also possible that isobutene could be formed from surface reactions as well. We note that selectivity to isobutene from *tert*-butanol across catalysts (lowest on RhCe, highest on Pt and PtCe) more closely matches the conversion than the temperature trends. Thus, at least some of the isobutene may come from surface reactions; although selectivity to isobutene may also be related to the ability of each catalyst to reform this intermediate.

It is also of interest that the activity of the catalysts toward C–O bond scission may be a factor in determining the conversion and selectivity trends of each catalyst. The Pt-containing catalysts may be more active for C–O bond scission [32], resulting in a higher conversion of *tert*-butanol. However, some of the initial dehydration of *tert*-butanol may also be homogeneous; the lower temperatures observed over the Rh-based catalysts (likely due to greater activity for endothermic reforming) may also result in lower initial conversion of the incoming fuel.

The other nonequilibrium product was acetone, which may have been produced in the gas phase by subsequent H and  $CH_3$  abstractions [26]. We also note that the negligible selectivity to  $CH_4$ ,  $C_2H_4$ and  $C_3H_6$  suggests that homogeneous decomposition of isobutene is not significant [33,25,34].

#### 4.3. Isobutanol

The main nonequilibrium products for isobutanol were isobutyraldehyde, propylene, and isobutene. Gas phase mechanisms for the production of these species are relatively straightforward, and closely reflect the patterns of 1-butanol and 2-butanol. Isobutene may have been produced by either molecular dehydration or by abstraction of H and OH radicals [26,29]. Sequential H abstractions



Fig. 7. Overall reaction pathways for butanol isomers. For brevity, only products with >5% selectivity are included. Arrow thickness indicates relative selectivity. Intermediate species may also adsorb to surface and react further. (a) 1-Butanol, (b) isobutanol, (c) 2-butanol and (d) *t*-butanol.

may have produced isobutyraldehyde, which in turn may have decomposed to propylene and syngas species [22]. Alternatively, propylene may have been produced either by abstraction of a primary H radical from isobutanol, followed by loss of a CH<sub>2</sub>OH radical, or by demethylation of the parent alcohol followed by abstraction of an OH radical [26,29].

PtCe and RhCe showed relatively high selectivities to the aldehyde and propylene, Rh showed relatively low selectivities to both, and Pt showed high selectivity for the aldehyde and low selectivity for propylene. As discussed above, these features cannot be explained solely by temperature effects, suggesting that some isobutyraldehyde and propylene are either produced or consumed on the catalyst surface.

# 4.4. Surface chemistry

Although the product spectra generally match a homogeneous mechanism well, surface reactions are certainly contributing to the observed products. Previous experiments have found that alcohols typically adsorb onto Pt and Rh surfaces by an oxygen lone pair, followed by O–H scission [35–42]. Surface reactions after this point may diverge on Pt and Rh [35], and to our knowledge have not been well studied on PtCe or RhCe. A feature shared by alcohol decomposition pathways on these surfaces is the dehydrogenation and decarbonylation of intermediate species, and desorption of H<sub>2</sub> and CO from the surface. Under certain conditions, intermediates may desorb [35,43], although we are unable to discern the relative contribution to the observed product spectrum with the current analytical setup.

It is also possible that intermediate carbonyl and olefin species formed in the gas phase are reacting on the catalyst surface. Under different conditions, Pt and Rh surface mechanisms for carbonyls have been found to be similar [35–39], and initial reactions in combustion of the primary and secondary butanols lead primarily to carbonyls that may react on the surface [23]. The actual situation is likely a convolution of the alcohol reacting on the surface and in the gas phase, vapor-phase intermediates reacting further in the gas phase and on the surface, and surface intermediates reacting further on the surface and desorbing to the gas phase, where they may or may not react further. To avoid unnecessary speculation, we have kept our proposed mechanisms as general as possible, proposing only what appear to be the dominant overall pathways based on observed products and intermediates with  $\geq$ 5% selectivity. Fig. 7 shows general reaction schemes for the CPO of each isomer.

# 4.5. Effect of catalyst

Trends for each alcohol were similar across the four catalysts studied, namely, high selectivity to CO and H<sub>2</sub> at low C/O ratios, steady selectivity to H<sub>2</sub>O and CO<sub>2</sub> across C/O ratios, and increasing selectivity to intermediate species (e.g. aldehydes and olefins) at high C/O ratios. However, the absolute selectivities were different across catalysts, with PtCe consistently exhibiting lower selectivity to CO and H<sub>2</sub> than the other catalysts. PtCe was conversely more selective for intermediate species than the other catalysts, particularly for 2-butanol and *iso*-butanol.

The observed temperature and syngas selectivity trends across catalysts appears to be related to endothermic reforming reactions of the feed alcohols and intermediate carbonyls and alkenes to CO and H<sub>2</sub>. The trend of selectivity for CO and H<sub>2</sub> across catalysts, in order of decreasing selectivity, was RhCe  $\approx$  Rh > Pt > PtCe, while the trend of catalyst backface temperature was generally PtCe > Pt > Rh  $\approx$  RhCe.

The addition of Ce likely has different effects for the Pt and Rh catalysts. For Pt, addition of Ce may lead to less active Pt centers by promoting bulk oxidation of the Pt metal, while the oxidation state of Rh (and hence the catalytic activity) is more sensitive to the surrounding environment than the presence of Ce [44]. In particular, the addition of Ce to Pt has been shown to inhibit oxidation of hydrocarbons [45], consistent with the relatively higher selectivity to olefins in the current experiments, and the observation that O<sub>2</sub> consumption was less than 100% over PtCe over some of the C/O range investigated for each alcohol. In the present experiments, it appears that adding Ce to Pt also inhibits reforming reactions, as discussed above, at least for small oxygenates and alkenes.

# 5. Conclusion

Primary and secondary alcohols decompose in the autothermal system mainly via a carbonyl intermediate in surface and homogeneous reactions. This result provides support to our previous proposal that molecules within in a functional group class behave similarly in a SCT reactor [16]. Tertiary alcohols, with no  $\alpha$ -H atom available for dehydrogenation, decompose by dehydration, although the lack of a dehydrogenation pathway does not necessarily lead to lower overall reactivity in an autothermal reactor.

Because of the similarity in trends across catalysts, it is difficult to discern relative contributions of homogeneous and heterogeneous reactions. The actual situation is likely a convolution of multiple reaction schemes, although some effect of catalyst is observed in the selectivities to CO and H<sub>2</sub>. To that end, our results are consistent with previous work [20,21] that found Pt and PtCe to be less active reforming catalysts than Rh and RhCe for these molecules, although as C/O approaches 0.8, all catalysts reform the alcohol isomers to an equilibrium syngas stream. Alternatively, as C/O approaches 2.0, high selectivities to carbonyls and light olefins, which are important chemical intermediates, are achieved.

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