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Partial oxidation of alcohols to produce hydrogen and chemicals in millisecond-contact time reactors

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Abstract

We compare the autothermal partial oxidation of 1-propanol and 2-propanol with methanol and ethanol on Rh with several additives in short-contact time reactors. All alcohols could produce H_2 at 70–90% selectivity, and Rh–Ce was superior to Rh in producing H_2. Methanol produced high conversion and high selectivity to H_2 even at high C/O where temperatures fell to $<600\,^\circ\mathrm{C}$. 2-Propanol gave lower conversions and less H_2 and CO than the other alcohols, but produced the most chemicals. Above $C/O = 1.5$, $\sim$70% of 2-propanol was converted into acetone or propylene. Up to 20% propylene was formed at $C/O = 1.5$. In contrast, 1-propanol gave <8% propylene and <15% propanal at any C/O and produced more ethylene than propylene. Much more oxygenates and olefins were formed on Rh than on Rh–Ce. These results show that different alcohols have very different selectivity in catalytic partial oxidation at short contact times even at high temperatures. Rapid adsorption of alcohols as alkoxy species leads to complete dissociation to H_2 and CO. Our results suggest that acetone and olefins likely were produced primarily by homogeneous reactions after all O_2 had been consumed in the catalyst. Although alkanes do not form significant oxygenates by partial oxidation at short contact times, alcohols can be made to produce predominantly oxygenates through suitable adjustments of C/O and catalyst.

Keywords: Partial oxidation; Methanol; Ethanol; 1-Propanol; 2-Propanol; Rh and Rh–Ce catalysts

1. Introduction

Biorefineries produce a myriad of products, including hydrogen for fuel cells and chemical feedstocks from renewable feedstocks. One possible approach to producing hydrogen and chemicals from biomass is the catalytic partial oxidation of biomass-derived liquids. Unlike fossil fuels, biomass-derived liquids contain many oxygenates that affect the performance of the reforming catalyst.

Previous research in our laboratory and other laboratories has focused on the autothermal reforming of ethanol and methanol [1,2]. Using contact times in the milliseconds (<10 ms), both methanol and ethanol have produced product streams containing high (85%) hydrogen selectivity at conversions exceeding 95%.

The present work examines the products and mechanism of partial oxidation of alcohols by examining the partial oxidation of the C_3 alcohols 1-propanol, which, like ethanol and methanol is a primary alcohol, and 2-propanol, a secondary alcohol.

1.1. Methanol reforming

Partial oxidation is an autothermal process that produces syngas from methanol [1,3]. Noble metal catalysts yield high activity and selectivity for syngas products. Using Pd/ZnO, a hydrogen selectivity of 96% and conversion of 70% were reported [3]. Pt and Rh catalysts on α-alumina monoliths gave lower hydrogen selectivities but higher conversions. Typical hydrogen selectivities were 65–75% with conversions >90% at lean C/O [1]. Very low (<1%) methane

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selectivity was observed, which is highly desired because methane consumes hydrogen and lowers the efficiency of reforming.

1.2. Ethanol reforming

The partial oxidation of ethanol produced 95% conversion and 85% hydrogen selectivity in an autothermal reformer using Rh–Ce [2]. When combined with Pt–Ce water–gas shift catalyst in a staged reactor, the hydrogen selectivity (based on hydrogen from ethanol) reached 130% with a 25 mol% ethanol and 75 mol% water mixture. This indicates that hydrogen was being formed from both ethanol and water in the autothermal reactor.

1.3. 1-Propanol and 2-propanol reforming

There have been few reports of the reforming of 1-propanol and 2-propanol [4]. The steam reforming of 2-propanol was investigated on Rh with various supports including CeO_2, Al_2O_3, SiO_2, ZrO_2, MgO, and TiO_2. Conversions $>90\%$ were obtained at temperatures of 400 °C at low space velocities. Rh–Ce produced the highest yields of syngas, which was suggested to be due to the oxygen storage capacity of ceria. Al_2O_3 and SiO_2 also produced high yields of syngas. ZrO_2, TiO_2, and MgO were less active to syngas, instead producing more acetone and propylene.

2. Experimental

2.1. Catalyst preparation

The catalyst coating procedure was as described previously [5]. The monoliths used were 80 or 45 pores per linear inch (ppi), made from α-alumina, 17 mm in diameter and 10 mm long, with a void fraction of ~ 0.8. Rh from $Rh(NO_3)_3$ solution was loaded to 5 wt% for Rh without additives. Monoliths with additives contained 2.5 wt% Rh and 2.5 wt% additive.

The additives used included ceria, cobalt, and ruthenium, all of which have been reported to promote syngas formation [2,6,7]. The catalyst and additive were deposited on the monolith concurrently. Ceria was prepared from $Ce(NO_3)_3 \cdot 6H_2O$, ruthenium from $RuCl_3 \cdot xH_2O$, and cobalt from $CoCl_2 \cdot 6H_2O$. After the monolith was loaded with catalyst, it was heated in air at 600 °C for 6 h to decompose the salts.

Pt was tested in a manner similar to Rh. However, Pt never achieved light-off or steady-state operation with either of the C_3 alcohols. This observation was consistent with results from previous experiments with ethanol [2].

2.2. Gas delivery and startup

Compressed air from cylinders and metered by mass flow controllers was used to provide oxygen for the partial oxidation reaction. The liquid fuels were delivered through an automotive fuel injector at the top of the quartz reactor. Heating tape wrapped around the quartz reactor above the catalyst provided heat to vaporize the fuel. The upstream temperature was maintained at 130–160 °C. Lightoff was achieved by flowing fuel and air over the catalyst and applying an external burner until the catalyst temperature reached ~ 800 °C. Once steady-state operation was obtained, no heat was applied to the reactor except to vaporize the fuel. No homogeneous ignition (flames) of the fuel before the catalyst was observed at conditions and temperatures shown.

2.3. Data acquisition and analysis

Most data were acquired at a total inlet flow rate, air plus fuel, of 4 standard liters per minute (slpm), although flow rates of 2 and 6 slpm were also examined. In all cases the data at 2 slpm showed lower conversions and lower selectivities to syngas because of lower reactor temperatures. At 6 slpm, high temperatures prevented the acquisition of data at low C/O due to the possibility of catalyst loss due to evaporation. The residence time of the gases in the catalytic monolith at 4 slpm was 10 ± 5 ms and the GHSV was $\sim 1 \times 10^5\ h^{-1}$. Data are presented as a function of C/O. This ratio was determined by dividing the number of carbon atoms in the fuel by the number of oxygen atoms from the air flowing into the reactor. Only oxygen atoms from the air were included, because only those atoms could oxidize the fuel. This was different from previous work [2] with ethanol in which the internal oxygen was included in the C/O calculation. Temperatures reported are regarded as accurate to ± 20 °C.

Gases were analyzed using gas chromatography by injecting samples with a gas syringe. All data points represent the average of three samples on a single catalyst. The data for Rh and Rh–Ce was repeated on a second catalyst. All results were reproducible within $\pm 5\%$. Selectivities reported were based on carbon atoms except for H_2, which was based on hydrogen atoms. No deactivation of catalyst activity was noted for time on stream of ~ 30 h with repeated shutdown and restart.

3. Results

3.1. Comparison of alcohols on Rh–Ce

Fig. 1 displays the conversion (a), temperature (b), hydrogen selectivity (c), and carbon monoxide selectivity (d) for methanol, ethanol, 1-propanol, and 2-propanol on Rh–Ce. Fig. 1a shows that methanol gave nearly complete conversion to products except at very rich C/O, where the temperature fell below 500 °C. The other primary alcohols both gave $>85\%$ conversion over the range of C/O tested. Finally, for all C/O, the secondary alcohol, 2-propanol, gave the lowest conversion. Fig. 1b shows that the reactor temperature increased with increasing alcohol chain length. The 2-propanol operated at a slightly higher temperature than the

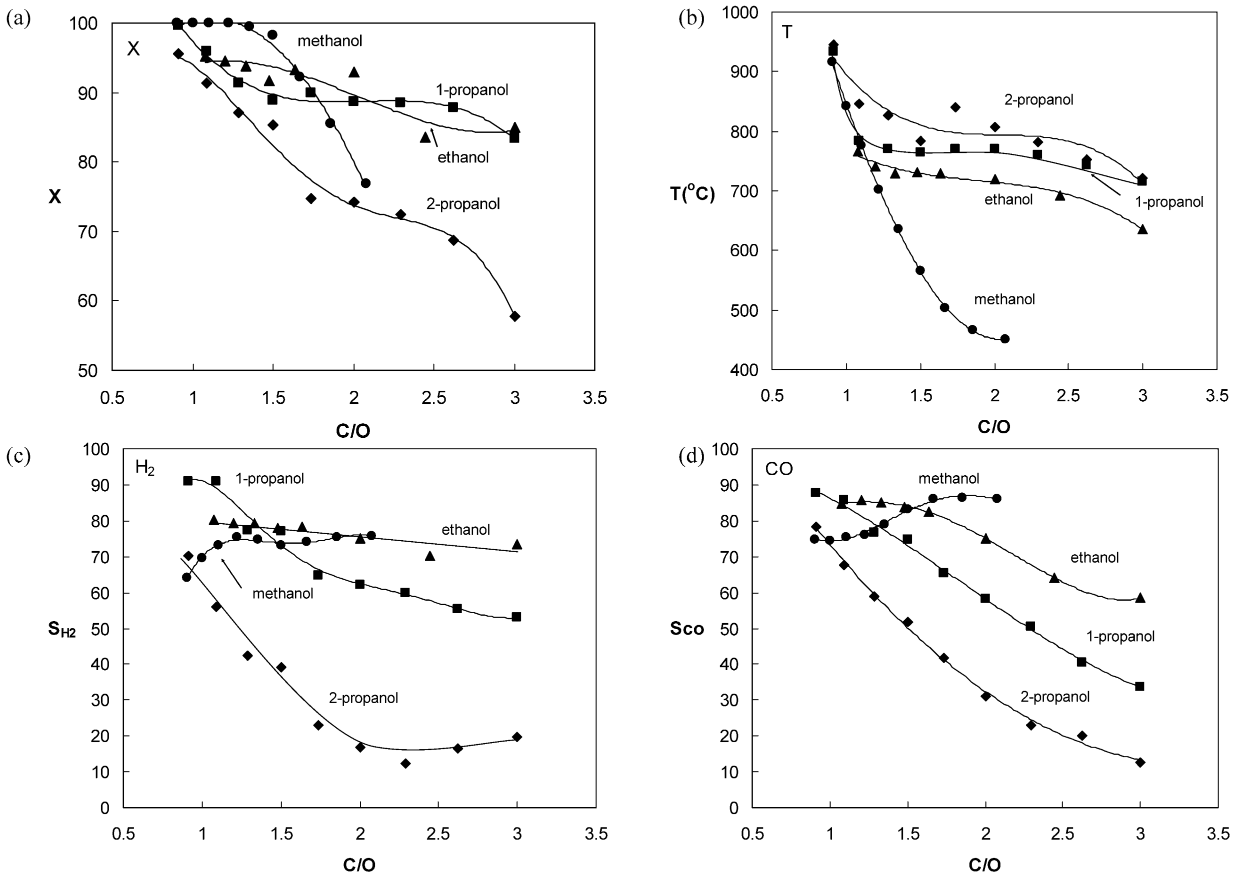

Fig. 1. Reactions of alcohols on Rh–Ce on a ceramic foam monolith at millisecond contact time. The conversion (a), reactor temperature (b), hydrogen selectivity (c), and carbon monoxide selectivity (d) are shown as a function of C/O ratio.

1-propanol. Figs. 1c and d display the hydrogen and carbon monoxide selectivities, respectively. Syngas was the favored product at low C/O for all the alcohols. The hydrogen and carbon monoxide selectivity indicates that with increasing carbon length, the alcohol produced less syngas and more of the other chemicals.

Fig. 2 shows the methane selectivity (a), ethylene selectivity (b), propylene selectivity (c), and sum of the selectivities observed for all C_2 and C_3 products for 1-propanol and 2-propanol (d). Fig. 2a shows that the methane selectivity remained $<5\%$ for all of the alcohols except ethanol, for which it was as high as 15% for high C/O. Fig. 2b shows the ethylene selectivity for ethanol, 1-propanol, and 2-propanol. Ethylene selectivities for ethanol and 2-propanol were $<2\%$ for all C/O, and 1-propanol showed high ethylene selectivity $\sim$20% at high C/O. Fig. 2c displays the propylene selectivity for 1-propanol and 2-propanol, showing that 2-propanol produced the most propylene with a maximum selectivity of 20% on Rh–Ce at high C/O and that propylene selectivity went through a maximum at a C/O of 1.5. At lower C/O, excess oxygen prevented the formation of propylene, and the syngas selectivity increased. At high C/O, the selectivity to acetone increased rapidly, which decreased the selectivity to propylene. Fig. 2d shows the sum of the C_2 and C_3 products of 1-propanol and 2-propanol. At all C/O, C_2 and C_3 products of 2-propanol were favored over those of 1-propanol.

3.2. *Role of catalyst in the partial oxidation of C_3 alcohols*

Fig. 3 shows the conversion (a), reactor temperature (b), hydrogen selectivity (c), and carbon monoxide selectivity (d) for 1-propanol. The conversion of 1-propanol was not strongly dependent on the additive used; nearly all conversions at a given C/O were within $\sim$5% of one another. Fig. 3b shows the reactor temperature for the different catalyst/additive combinations. At lean C/O, there was wide variability in the temperature, with Rh and Rh–Ru operating at high temperatures and Rh–Ce significantly lower ($\sim$200 °C). This was due to more combustion on Rh and Rh–Ru at low C/O. However, as the C/O increased, the temperatures became closer, as less oxygen was available for combustion. Figs. 3c and d show the selectivities for hydrogen and carbon monoxide. The best syngas catalyst was Rh–Ce; the carbon monoxide selectivity was $\sim$10% higher for Rh–Ce, and hydrogen selectivity was even higher.

Fig. 4 shows a more detailed examination of Rh and Rh–Ce for 1-propanol. The selectivities for carbon monoxide, propylene, ethylene, and propanal are shown. Rh–Ce produced more carbon monoxide than Rh, presumably be-

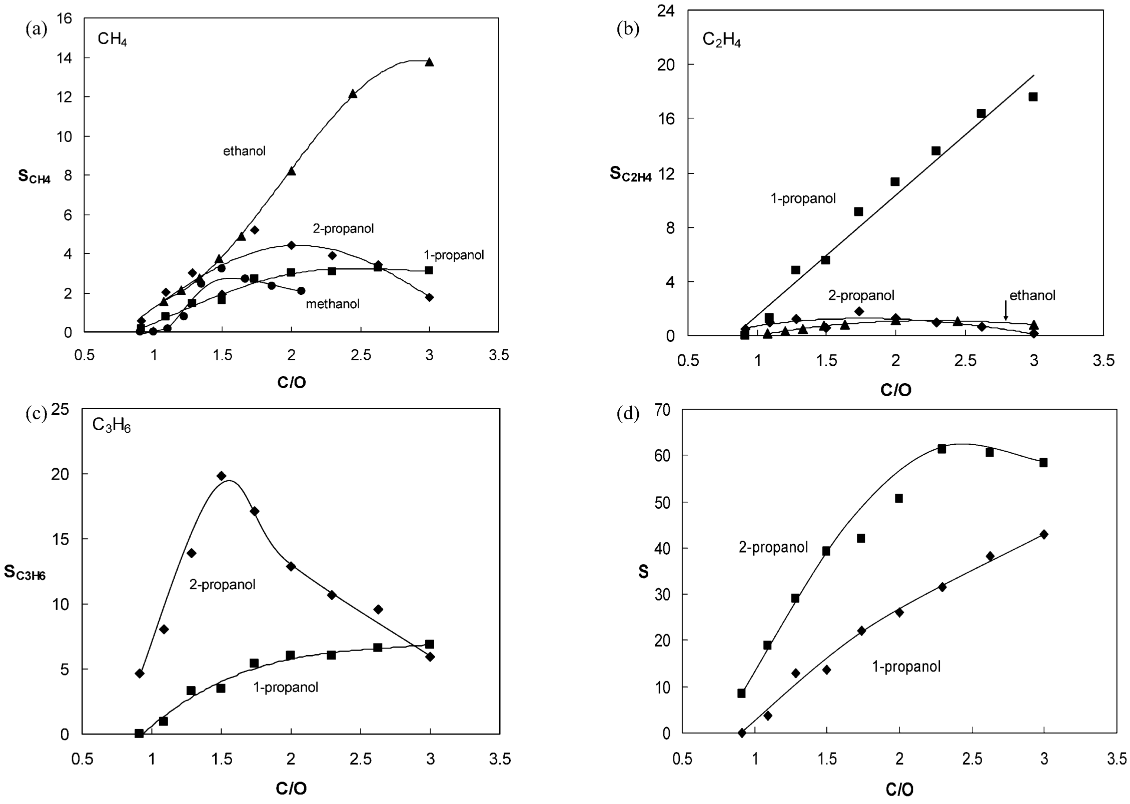

Fig. 2. Reactions of alcohols on Rh–Ce on a ceramic foam monolith at millisecond contact time. The methane selectivity (a), ethylene selectivity (b), propylene selectivity (c), and sum of the C_2 and C_3 product selectivities from 1- and 2-propanol (d) are shown as a function of C/O ratio.

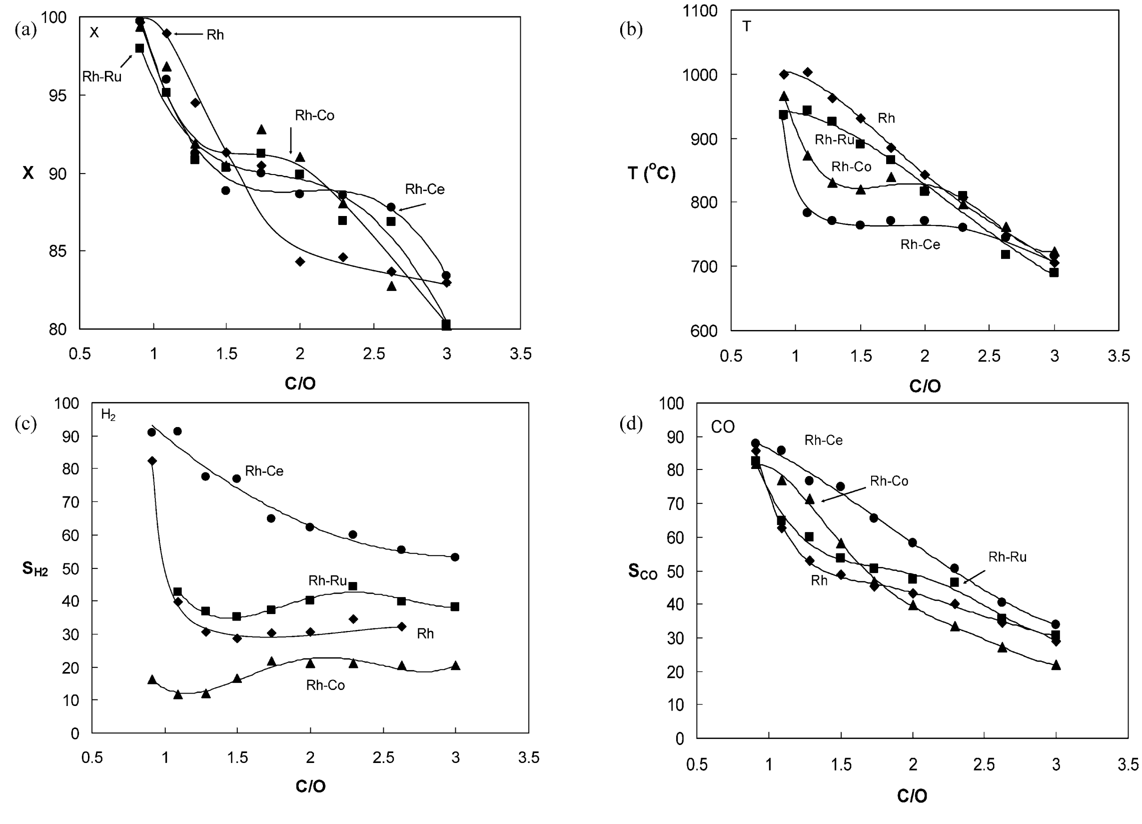

Fig. 3. Comparison of Rh, Rh–Ce, Rh–Ru, and Rh–Co for 1-propanol at millisecond contact time. The conversion (a), reactor temperature (b), hydrogen selectivity (c), and carbon monoxide selectivity (d) are shown as a function of C/O ratio.

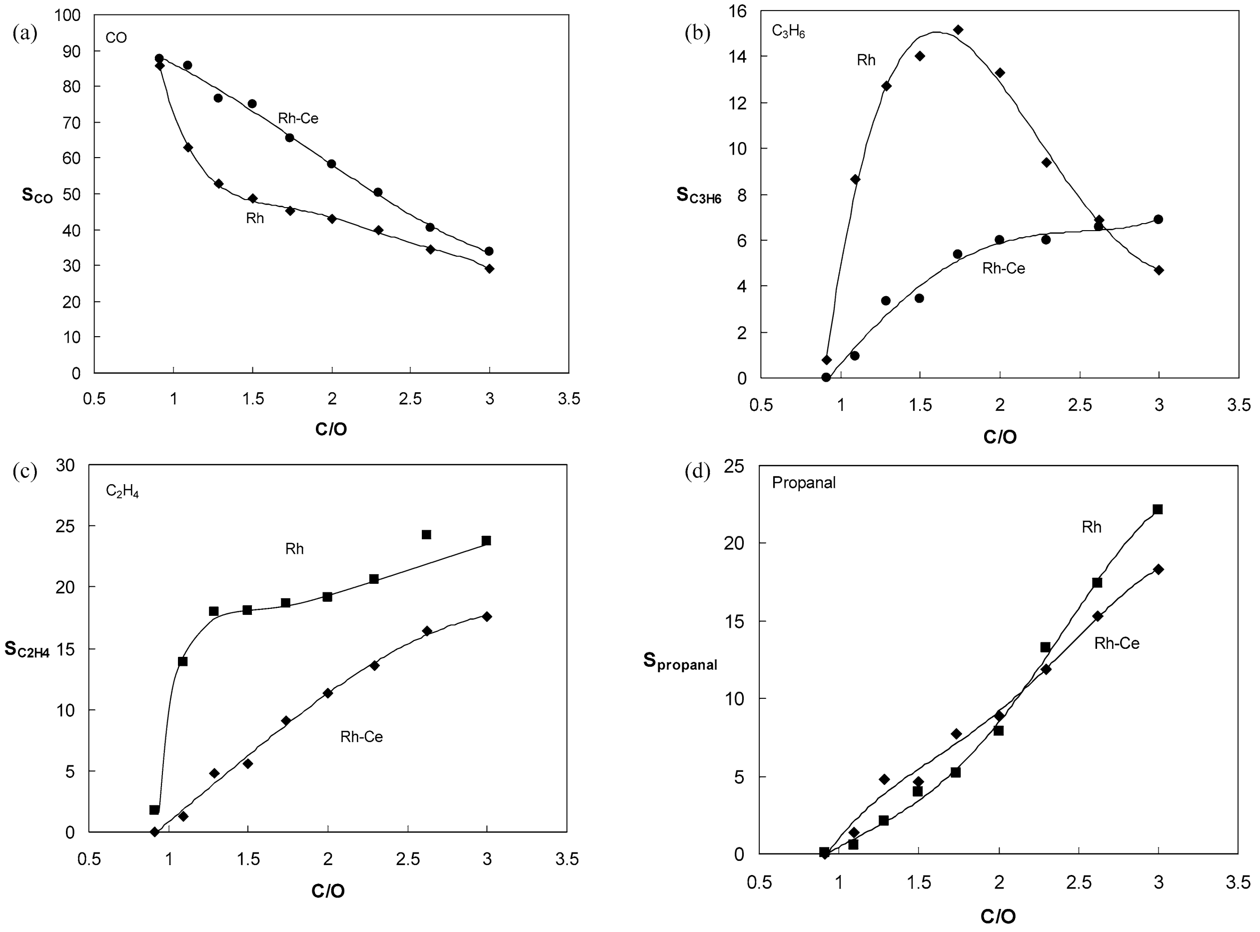

Fig. 4. Comparison of Rh and Rh–Ce for 1-propanol at millisecond contact time. The carbon monoxide selectivity (a), propylene selectivity (b), ethylene selectivity (c), and propanal selectivity (d) are shown as a function of C/O ratio.

cause Ce stores oxygen and makes it available for reaction via a redox reaction. Rh produced more ethylene and propylene. Both catalysts produced approximately the same amount of propanal.

Fig. 5 shows the conversion (a), reactor temperature (b), hydrogen selectivity (c), and carbon monoxide selectivity (d) for 2-propanol. The conversion of 2-propanol did not vary much on Rh–Ru, Rh–Ce, and Rh but was ∼10% lower on Rh–Co. The conversions for all catalysts were lower than those for 1-propanol. Fig. 5b shows the reactor temperature for the different catalyst/additive combinations. At lean C/O, there was wide variability in the temperature, with Rh and Rh–Ru operating at high temperatures and Rh–Ce and Rh–Co operating at significantly lower temperatures. Figs. 5c and d show the selectivities to hydrogen and carbon monoxide for the four different catalysts. Rh–Ce and Rh–Co were the best hydrogen catalysts at lean C/O, whereas all of the catalysts but Rh produced approximately the same carbon monoxide selectivity.

Fig. 6 shows a more detailed examination of Rh and Rh–Ce for 2-propanol. Selectivities for carbon monoxide, propylene, and acetone are shown. Rh–Ce produced more carbon monoxide at low C/O than Rh. As with 1-propanol, this was due to the oxygen storage capability of ceria. Rh produced ∼5% more propylene and ∼10% more acetone. The propylene selectivity goes through a peak at $C/O = 1.5–1.7$ due to high syngas selectivity at low C/O and high acetone selectivity at high C/O.

3.3. Pore size and preheat

Fig. 7 shows the effect of pore size on the partial oxidation of 1-propanol and 2-propanol. The carbon monoxide selectivity (a) and propanal selectivity (b) are shown for 1-propanol, and carbon monoxide selectivity (c) and acetone selectivity (d) are shown for 2-propanol. The 80-ppi monolith had more surface area and active catalytic sites available for reaction. The carbon monoxide and hydrogen selectivities for both 1-propanol and 2-propanol were higher for the 80-ppi monolith. This indicates that higher-surface area catalysts yield more syngas products. The olefin and oxygenate selectivities were higher for the 45-ppi monolith, however. This suggests that more complex chemical products were produced by homogeneous reactions.

Fig. 8 shows the temperature (a), carbon monoxide selectivity (b), and propanal selectivity (c) for two preheat temperatures, 160 and 260 °C. The catalyst was Rh–Ce, and the

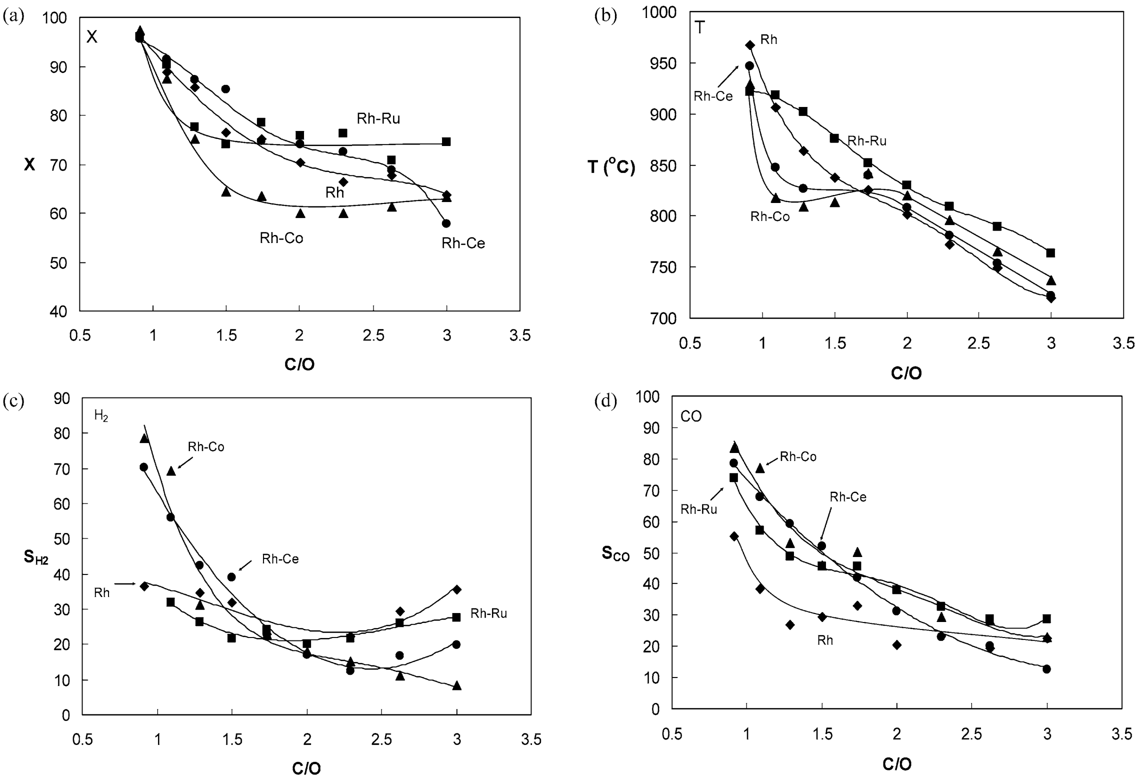

Fig. 5. Comparison of Rh, Rh–Ce, Rh–Ru, and Rh–Co for 2-propanol at millisecond contact time. The conversion (a), reactor temperature (b), hydrogen selectivity (c), and carbon monoxide selectivity (d) are shown as a function of C/O ratio.

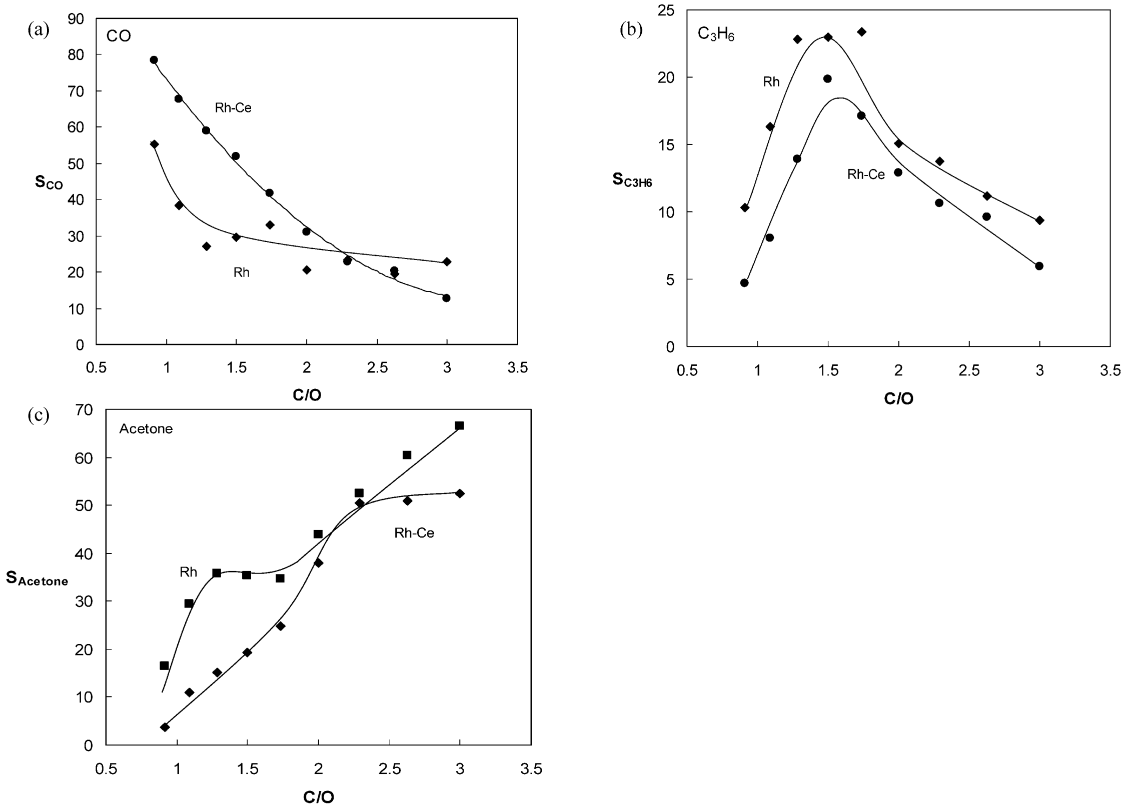

Fig. 6. Comparison of Rh and Rh–Ce for 2-propanol at millisecond contact time. The carbon monoxide selectivity (a), propylene selectivity (b), and acetone selectivity (c) are shown as a function of C/O ratio.

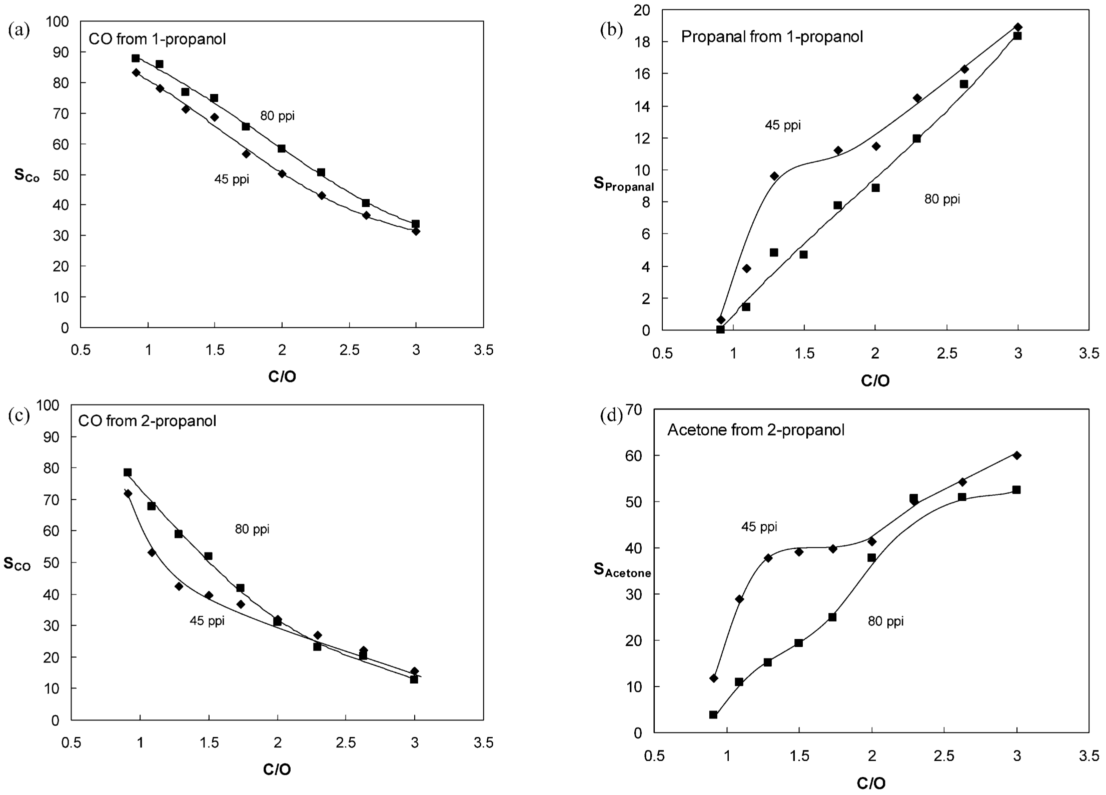

Fig. 7. Comparison of catalyst pore size on reaction products. The catalyst used was Rh–Ce for 80 ppi monoliths and 45 ppi monoliths. The carbon monoxide selectivity (a) and propanal selectivity (b) are shown for 1-propanol as a function of C/O ratio. The carbon monoxide selectivity (c) and acetone selectivity (d) are shown for 2-propanol as a function of C/O ratio.

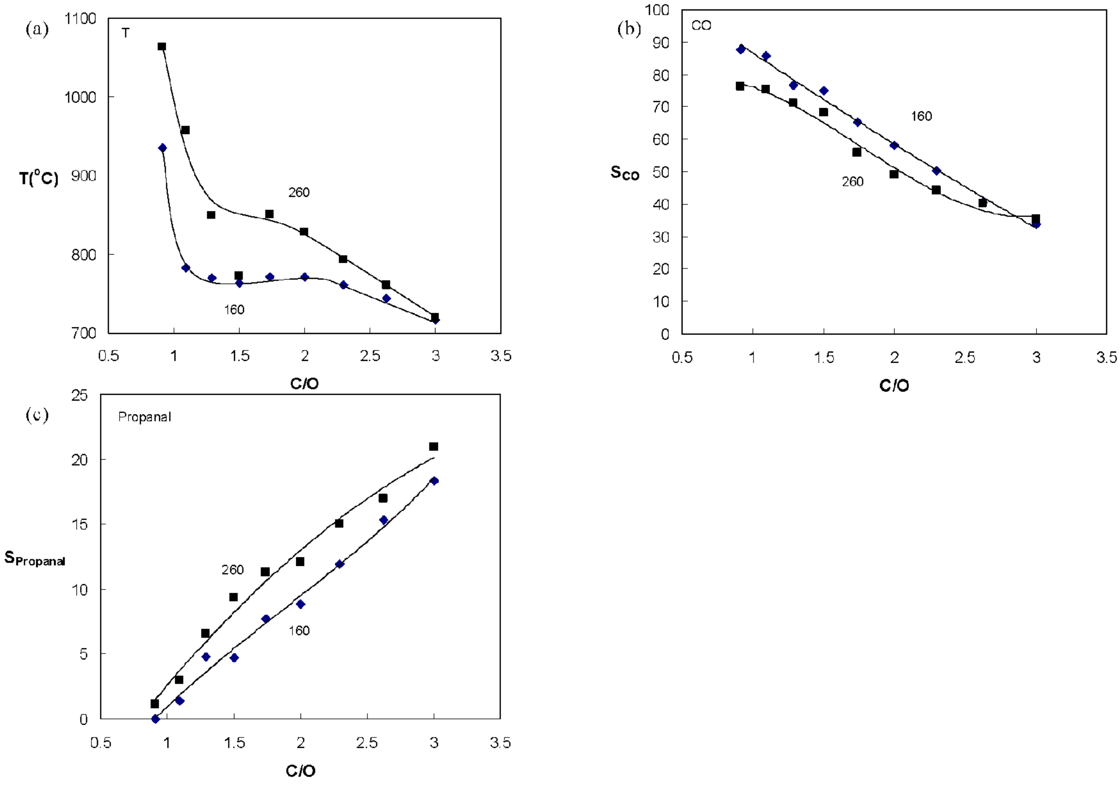

Fig. 8. Comparing the effect of preheat on reaction products. The fuel was 1-propanol and the catalyst used was Rh–Ce. Two preheat temperatures were tested: 160 and 260 °C. The temperature (a), carbon monoxide selectivity (b), and propanal selectivity (c) are shown as a function of C/O ratio.

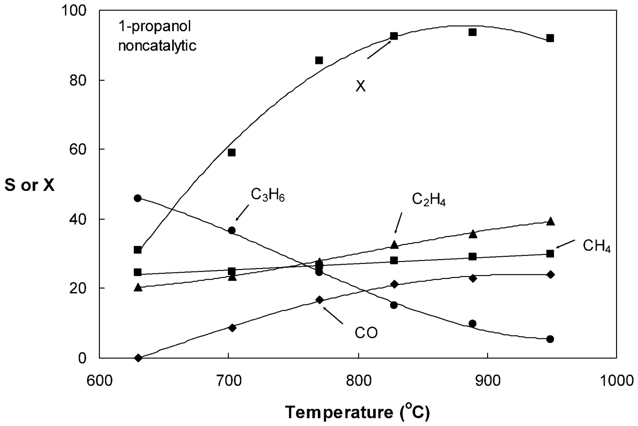

Fig. 9. The conversion and selectivities of 1-propanol in a tube with a noncatalytic monolith foam. The figure shows the conversion, carbon monoxide, ethylene, propylene, and methane selectivities as a function of temperature in a heated tube with no catalyst. The experiment simulated the homogeneous pyrolysis of 1-propanol. For these experiments the heated zone of the tube was ∼30 cm, so the residence time was ∼200 ms.

fuel was 1-propanol. Increasing the preheat temperature led to higher reactor temperatures, which in turn favored more homogeneous reactions, shown by the higher propanal selectivity. Conversely, less heterogeneous reactions occurred at higher temperatures, shown by the lower carbon monoxide selectivity.

3.4. Noncatalytic monolith

A noncatalytic monolith test was performed to study the role of homogeneous chemistry in the partial oxidation of the C_3 alcohols. An uncoated, α-Al_2O_3 monolith was placed inside a quartz tube, and 1-propanol and nitrogen were flowed through the tube at a flow rate of 4 slpm. A furnace was used to regulate the temperature. The heated zone in the furnace was ∼30 cm long, and residence time of the gases was 150–300 ms. Temperatures tested ranged from 600 to 950 °C. These conditions simulated the downstream portion of the catalyst where no oxygen is present and only homogeneous reactions producing olefins and oxygenates can occur.

The homogeneous chemistry of ethanol has been examined in a noncatalytic monolith experiment [8] and compared with the results from a homogeneous combustion and pyrolysis model [9]. Four parameters affecting the homogeneous chemistry of ethanol decomposition were modeled. First, homogeneous chemistry with oxygen and without oxygen was tested to examine the effect of oxygen on reaction chemistry. Second, two temperatures (600 and 900 °C) were modeled to examine temperature effects. Third, residence times of 200 and 600 ms were tested, because the homogeneous kinetics showed no reaction at 600 °C at 200 ms. Finally, for experiments with oxygen, C/O was varied between 0.7 and 1.3.

Fig. 9 shows the results of an experiment in which nitrogen and 1-propanol were flowed over the reactor with only an α-Al_2O_3 monolith with no catalyst. At temperatures >800 °C, 1-propanol conversions were >90%. However, the conversion fell considerably <800 °C and dropped to 30% at ∼650 °C. The primary products from pyrolysis are ethylene, propylene, methane, and carbon monoxide (from the CO present in 1-propanol). Both ethylene and methane are relatively constant, with selectivities between 20 and 35% throughout the temperature range tested. However, propylene and CO vary widely. Propylene is favored at low temperatures, with ∼45% selectivity at 650 °C but only ∼5% selectivity at 950 °C. This decrease is offset by an increase in CO selectivity from ∼0 to 20% at high temperatures. Hydrogen selectivity behaved very much the same as CO selectivity, reaching 25% at high temperatures and falling to <5% at low temperatures.

One surprising result was the absence of propanal. Even at high temperatures, propanal selectivity remained <1%. High selectivity of acetaldehyde from ethanol was observed when air was fed to the reactor and in the modeling of the pyrolysis of ethanol [8]. This suggests that aldehydes are formed with oxygen-assisted reactions.

3.5. Acetone

Acetone was flowed over Rh and Rh–Ce monoliths at 4 slpm because of the high selectivity to acetone (>50%) observed from 2-propanol. Acetone gave low conversion at virtually all C/O levels. At $C/O = 1.5$, the conversion was ∼70%; at high C/O, it fell to <40%. The products were virtually all syngas and methane; no C_2 or C_3 products were observed. The lack of olefins and oxygenated products is believed to be due to the absence of any weak α-C–H bonds. This absence impedes homogeneous chemistry, the mechanism for the production of olefins and oxygenates.

4. Discussion

A major result from these experiments is that selectivity varies considerably among the alcohols. In contrast, all alkanes can be made to produce primarily syngas at low C/O and olefins at higher C/O. No oxygenates (much <1%) are ever observed with alkanes, except for the single gauze reactor [10], where surface reactions produce heat that drives homogeneous combustion reactions in an empty tube.

Our general model of these processes in short-contact time reactors is that high-velocity premixed gases at low temperature force surface reactions early in the hot catalyst (typically within the first millimeter), and all oxygen is consumed within at least a few millimeters of the catalyst entrance. Surface reactions of all fuels appear to form mostly C_1 products (CO, CO_2, and CH_4) and H_2 and H_2O.

After all of the O_2 is consumed, homogeneous reactions appear to dominate. For $C/O <1$, most fuel reacts in the oxidation zone, and C_1 products form exclusively. Homogeneous reactions occur primarily downstream in the channels of the monolith and after the monolith. Detailed modeling of these reaction systems [11] shows that the Rh catalyst in the oxidation zone contains primarily oxygen atoms, whereas surface carbon dominates downstream in the catalyst. Carbon covered surfaces are probably inert toward any surface reactions, so that in this zone the effect of the monolith surface appears to be primarily to maintain high and uniform temperatures by solid heat conduction.

Temperature is a critical parameter in controlling rates of surface and homogeneous reactions, which in turn control selectivity. Measured temperatures are at the exit of the catalyst, and these and other experiments have shown that maximum temperatures are 100–200 °C higher than at the exit. The highest temperatures occur near the entrance of the monolith, where most surface reactions occur. Following the monolith, rapid cooling of the product gases rapidly quenches all reactions and freezes the product mixture formed within the monolith.

4.1. *Surface reactions of alcohols*

Alcohol adsorption and decomposition on many noble metal surfaces [12,13], including Rh [12], has been examined extensively on well-defined single-crystal surfaces. For example, the decomposition of ethanol and acetaldehyde have been studied on Rh(111) [12]. It appears that ethanol adsorbs, forming an ethoxy species. The next step is the formation of a bridged oxametallacycle, which readily undergoes C–C bond scission. The resulting species quickly break down to adsorbed C, H, and O atoms, which recombine to form syngas. However, acetaldehyde adsorbs on two adjacent Rh sites, forming an η^2-acetaldehyde species that undergoes C–C bond scission to form carbon monoxide and methyl, which can then form methane [12].

We note that at our surface temperatures (800–1000 °C), noble metals are predicted to be essentially clean even at atmospheric pressure. All experiments agree that alcohols adsorb initially through the lone pair of electrons on the O atom, and that above 200 °C, rapid dissociation occurs to form the alkoxy species

$$\mathrm{ROH} \rightarrow \mathrm{ROH(s)} \rightarrow \mathrm{RO(s)} + \mathrm{H(s)}.$$

The adsorbed alkoxy is stable under UHV conditions to ~300 °C [12], where it is observed to decompose completely to adsorbed C, H, and O atoms and CO. This is in agreement with the present results showing that CO and H_2 dominate, with CO_2 and H_2O as minor products at low C/O.

Although dehydration of alcohols can yield olefins, the alkoxy species do not have obvious dehydration channels available. Thus other pathways probably would be needed to produce olefins on the surface.

From methanol, there are no reaction channels of methoxy that yield higher species, except perhaps dimerization. Ethoxy could dissociate with addition of adsorbed H to ethane (<0.5% observed) or removal of H to form ethylene (<2% observed). 1-propanol forms propoxy, which could dissociate to form propane, propylene, or ethylene. We observe more ethylene than propylene, which could occur through a surface reaction,

$$\mathrm{C_3H_7O(s)} \rightarrow \mathrm{C_2H_4} + \mathrm{CH_3O(s)}$$

or

$$\mathrm{C_3H_7O(s)} \rightarrow \mathrm{C_3H_6} + \mathrm{OH(s)},$$

although scission of the C–O bond to make propylene should be more difficult than scission of the C–C bond to make ethylene.

We know of no surface science studies of 2-propanol, but steric limitations should make it less reactive than 1-propanol (which would lead to more homogeneous chemistry), and there are no obvious surface reaction channels that would yield olefins. The α-C–H bond in absorbed isopropoxy may be weaker than other bonds, which could lead to acetone by a surface reaction,

$$\mathrm{C_3H_7O(s)} \rightarrow \mathrm{CH_3COCH_3} + \mathrm{H(s)}.$$

We suggest that surface reactions of all alcohols should lead to mostly C_1 products, and that species larger than C_1 products are probably formed by homogeneous reactions.

4.2. *Homogeneous reactions*

The combustion chemistry of ethanol [9] and methanol [14] has been studied extensively, and detailed reaction mechanisms of ethanol oxidation involving 57 species and more than 370 reactions are available [9]. No detailed mechanisms appear to be available for the combustion of C_3 alcohols.

The experiments in Fig. 9 using a tube without a catalyst show that nearly complete conversion of 1-propanol can be obtained above 800 °C, even in the absence of O_2, although it should be noted that in a tube furnace the reactants are heated for nearly the entire length of the furnace, so that the residence time in this experiment is ~200 ms, compared to 10 ms in the catalytic monolith, where the gases are cool before they reach the catalyst and reaction is complete.

Fig. 9 shows that the major products from homogeneous reactions are C_2H_4, C_3H_6, CH_4, and CO, with less propylene and more dissociative products at high temperatures. The H_2 selectivity was 25%, and CO was ~20% at the highest temperatures.

Selectivities were predicted using the detailed model for ethanol and for ethanol–O_2 mixtures as functions of time and temperature. They show that low C/O, high temperatures, and high residence times favor syngas formation. For example, at 900 °C and 200 ms, the CO selectivity falls from 60% at $C/O = 0.7$ to <40% at $C/O = 1.3$. Ethylene formation accounts for the decrease in CO selectivity as ethylene selectivity increases from ~10% at low C/O to 35% at rich C/O. This is in contrast to 600 °C, which showed very little conversion (<1%) even at long residence times of 600 ms.

4.3. Effects of catalyst and additives

The results of Fig. 3 clearly show that Rh–Ce is the best catalyst for H_2 and CO while suppressing higher products, and that Rh and Rh–Co produce much less H_2 and CO while enhancing higher products. Similar trends are observed with all alcohols, although methanol produces no higher compounds and ethanol very little.

Conversions on all catalysts are high and approximately the same, although temperatures vary widely, with Rh being 200 °C hotter than Rh–Ce, which was the coldest. Temperatures correlate with selectivities because the catalyst producing most CO_2 and H_2O will, of course, run hotter. This can, in turn, generate more products of homogeneous chemistry.

There are large differences between Rh and Rh–Ce for higher products. For example, with 1-propanol at $C/O = 1.4$, the C_2H_4 is 3% on Rh–Ce and 17% on Rh and the C_3H_6 is 3% on Rh–Ce and 15% on Rh. Acetaldehyde formation from 1-propanol appears to be essentially the same on Rh and Rh–Ce.

5. Conclusions

The selectivity of catalytic partial oxidation of alcohols varies strongly with size and structure of the alcohol and with the catalyst used. We examined only a few catalysts and reaction parameters in the present study, because our interest was in exploring the mechanisms rather than optimizing for a particular product. Methanol and ethanol produce essentially only H_2 and CO, because they react rapidly on the surface, and the alkoxy species probably has no surface reaction channels that do not lead to total decomposition on noble metal surfaces. Propanol and (probably) higher alcohols have many surface and homogeneous reaction channels that can lead to large amounts of larger products, and these systems often can be tuned to produce a single dominant product, such as acetone from 2-propanol. Short-contact time reactors can be tuned to exhibit high selectivities to specific products, even at very high temperatures. The patterns of reaction can be adjusted strongly by changing catalyst, feed, and flow conditions, and at short contact times these product distributions are frozen to yield simple, and perhaps valuable, product distributions.

Acknowledgments

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