



December 2004

# A Comparison of Ceria and Sm-Doped Ceria for Hydrocarbon Oxidation Reactions

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## Recommended Citation

Zhao, S., & Gorte, R. J. (2004). A Comparison of Ceria and Sm-Doped Ceria for Hydrocarbon Oxidation Reactions. Retrieved from [http://repository.upenn.edu/cbe\\_papers/59](http://repository.upenn.edu/cbe_papers/59)

Postprint version. Published in *Applied Catalysis A: General*, Volume 277, Issues 1-2, 8 December 2004, pages 129-136.  
Publisher URL: <http://dx.doi.org/10.1016/j.apcata.2004.09.003>

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## Keywords

ceria, samaria, samaria-doped ceria (SDC), methane oxidation, ethane oxidation, propane oxidation, *n*-butane oxidation, kinetic-isotope effect

## Comments

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## A Comparison of Ceria and Sm-Doped Ceria for Hydrocarbon Oxidation Reactions

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### Abstract

The oxidation of methane, ethane, propane, and n-butane has been studied over  $\text{CeO}_2$  and  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_x$  (SDC) catalysts. The rates for methane and ethane were found to be indistinguishable over the two catalysts, while the rates for propane and n-butane were much higher on ceria compared to SDC. The difference between n-butane oxidation over ceria and SDC is shown to result from a low-temperature rate process on ceria that is not present on SDC. Measurements using  $\text{CD}_4$  and  $\text{C}_4\text{D}_{10}$  show that both low- and high-temperature rates exhibit a similar kinetic-isotope effect; however, the low-temperature process is half-order in  $\text{O}_2$ , while the high-temperature process is zeroth-order. Pulse studies demonstrate that oxygen from the bulk becomes accessible for reaction at approximately the same temperature as that at which the high-temperature rate process becomes important. The implications of these results for understanding the effect of doping on reactions over ceria, and for characterization of oxides using standard test reactions, are discussed.

**Key Words:** ceria; samaria; samaria-doped ceria (SDC); methane oxidation; ethane oxidation; propane oxidation; n-butane oxidation; kinetic-isotope effect.

## Introduction

Among oxides, ceria is one of the better hydrocarbon oxidation catalysts [1,2], a property associated with the relative ease with which Ce can go from  $\text{Ce}^{+4}$  to  $\text{Ce}^{+3}$ . A particularly intriguing aspect of ceria is the fact that one can modify its properties dramatically by high-temperature aging [3-5], an important consideration for Oxygen-Storage Capacity (OSC) in three-way automotive catalysts. To maintain activity in the automotive application, it is essential that ceria be stabilized by mixing it with zirconia [6]. Although the mechanism by which zirconia stabilizes ceria is still not well understood, it has been shown that ceria films deposited onto zirconia substrates are much more easily reduced than ceria films deposited onto alumina, apparently because zirconia directs the structure of  $\text{CeO}_2$  films [7]. The catalytic activity and ionic conductivity of  $\text{CeO}_2$  can also be modified by doping with  $\text{Gd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ , or  $\text{La}_2\text{O}_3$  [8-13], again because of what these ions do to the structure of ceria. For example, the increased ionic conductivity observed with Gd- and Sm-doped  $\text{CeO}_2$  is due to stabilization of the cubic, fluorite structure with oxygen vacancies [8]. However, a detailed understanding of how dopants and structure affect the catalytic properties of ceria is still missing.

While it is often suggested that doping ceria should increase its activity for oxidation chemistry, recent studies from our laboratory have found that many dopants to  $\text{CeO}_2$ , including  $\text{Yb}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ , or  $\text{Pr}_6\text{O}_{11}$ , significantly decrease the catalytic activity for butane oxidation [14,15]. For example, butane-oxidation rates measured at 650 K on  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ ,  $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ , or  $\text{La}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  were more than 100 times lower than that on pure  $\text{CeO}_2$ . Each of these mixed oxides was shown to be a solid solution based on shifts in the lattice parameter obtained using XRD; and the decreased rates could not be explained by lower surface areas or by segregation of the dopant to the surface of the  $\text{CeO}_2$ . Experiments performed with lower Sm and Gd doping levels indicated that large decreases in rate were observed even with  $\text{Sm}_{0.05}\text{Ce}_{0.95}\text{O}_{1.975}$  and  $\text{Gd}_{0.05}\text{Ce}_{0.95}\text{O}_{1.975}$ .

In the present study, we investigated the catalytic properties of Sm-doped ceria more carefully in order to better understand how dopants affect catalytic properties. We chose Sm doping for this study because, among rare-earth dopants, Sm causes the largest increase in ionic conductivity in ceria [8] and also causes the biggest decrease in activity for n-butane oxidation [14]. We will show that the effect that Sm has on catalytic properties of ceria depends on what the reactant is, with methane and ethane showing very different results compared to propane and

n-butane. Based on our present results, we suggest that there is a distinct, low-temperature rate process for oxidation of propane and n-butane on  $\text{CeO}_2$  that is associated with oxidation and reduction of the first monolayer of ceria. The addition of  $\text{Sm}^{+3}$  removes this rate process.

## Experimental

The samples were from the same batch as two of the samples used in our previous study [14]. Pure ceria was obtained by decomposing  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 99.5% purity) in air at 873 K. To prepare the Sm-doped ceria (SDC) in the form of a solid solution, we first dissolved  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 99.9) in distilled water at the desired Sm:Ce mole ratio of 0.2:0.8, dried the mixture at 373 K, and then heated the mixed salt to 873 K in air. The lattice parameter of the SDC sample, determined using XRD, was 0.544 nm, a value consistent with the formation of a solid solution [8]. Furthermore, our previous study showed that samples made by co-precipitation of  $\text{Sm}_2\text{O}_3$  and  $\text{CeO}_2$  using ammonia gave exactly the same catalytic results [14]. The surface areas of the ceria and SDC samples were calculated from BET isotherms and found to be  $61 \text{ m}^2/\text{g}$  for the ceria and  $36 \text{ m}^2/\text{g}$  for the SDC, after outgassing at 673 K. BET measurements performed after carrying out rate measurements demonstrated that the surface areas did not change under the conditions used in this study.

Hydrocarbon oxidation rates were measured in a ¼-inch, Pyrex, tubular reactor, operating at atmospheric pressure, using 0.10 g of sample. The partial pressures of the reactants were controlled by adjusting the volumetric flow rates of the hydrocarbons,  $\text{O}_2$ , and He; and the rates were determined under differential reaction conditions, with the conversion of the limiting reactant being less than 10% for all rate measurements. The compositions of the gases leaving the reactor were determined using a gas chromatograph (SRI8610C) equipped with a Hayesep Q column and a TCD detector. To avoid potential complications associated with water, the analysis of the products was performed on a dry basis after removing water in trap held at 273 K. Under the conditions used in this study, the only reaction products observed in significant quantities were  $\text{CO}_2$  and water.

Light-off curves for the hydrocarbon-oxidation reactions were measured in a similar flow reactor but the product analysis was performed using a quadrupole mass spectrometer. In all cases, the temperature ramp rate was fixed at 10 K/min. To account for the difference in surface areas of ceria and SDC, the reactor was loaded with either 0.1 g of ceria or 0.17 g of SDC. In addition to reaction measurements with regular hydrocarbons, measurements were performed

with C<sub>4</sub>D<sub>10</sub> (n-butane-d<sub>10</sub>, Sigma Aldrich) and CD<sub>4</sub> (methane-d<sub>4</sub>, Sigma Aldrich) to gain insight into the rate-limiting steps for oxidation of methane and n-butane.

The transient-pulse experiments were performed on another flow reactor that has computer-controlled solenoid valves that allow step changes in the composition of reactants. The product gases leaving the reactor were again analyzed using a quadruple mass spectrometer. Integration of the partial pressures as a function of time allowed accurate determination of the amounts of oxygen that could be added or removed from the under various reaction conditions. The amount of catalyst used in the pulse studies was 1.0 g and the total gas flow rate was maintained at 100 ml/min.

The FTIR spectra were recorded using a Mattson Galaxy FTIR spectrometer with a diffuse-reflectance attachment, Collector II<sup>TM</sup>, provided by Spectra-Tech Inc. This system allowed spectra to be collected between room temperature and 873 K, with flowing gases of any desired composition. The samples were placed inside the chamber without packing or dilution. Spectra were taken in He after exposure the oxidized sample to 25 torr n-butane at 723 K for 30 min and after exposure to the flowing oxygen. A total of 256 scans were accumulated in each measurement at the resolution 2 cm<sup>-1</sup>.

## Results

### *Hydrocarbon Oxidation Rates*

In our previous paper [14], the oxidation rates for n-butane were shown to be significantly lower on SDC compared to pure ceria. To determine whether this difference in activity depends on the nature of the hydrocarbon, we compared oxidation rates over the two catalysts for methane, ethane, propane, and n-butane, with the results shown in Fig. 1 and tabulated in Table 1. The rates in this figure have been normalized to account for the difference in surface areas of the two samples. Since we were only able to maintain differential reaction conditions over a limited range of rates, the higher activities are associated with the sample that shows a given rate at a lower temperature. As shown in Figs. 1a) and 1b), the reaction rates over ceria and SDC were indistinguishable for both methane and ethane. It is also noteworthy that the absolute rates and activation energies for methane and ethane are similar. Since the reaction rates for ethane were slightly higher than for methane and almost twice as much O<sub>2</sub> is consumed in the oxidation of ethane, these rates cannot be limited by O<sub>2</sub> adsorption.

Figs. 1c) and 1d) demonstrate that reaction rates over ceria and SDC are very different for propane and n-butane, with the rates becoming significant at much lower temperatures on ceria compared to SDC. For SDC, a specific rate for propane and n-butane occurs at a similar temperature as for methane and ethane under the conditions of these experiments. Given the differences in partial pressures and in the activation energies of the oxidation rates for the different hydrocarbons, the similarity may be circumstantial; however, the result is in sharp contrast to that observed for the ceria catalyst. Over ceria, the oxidation rates for propane and n-butane were much higher than for methane and ethane. The activation energies for oxidation of propane and n-butane were also lower than the activation energies for methane and ethane over both catalysts.

To determine whether the conclusions about the relative rates might be different at higher conversions, we performed light-off measurements with methane and n-butane, using the same reactant partial pressures as used in the experiments of Fig. 1, with the results shown in Fig. 2. The data in Fig. 2a) demonstrate that the conversions for methane on ceria and SDC were essentially indistinguishable over the entire temperature and conversion range, in agreement with rate data in Fig. 1a). In contrast, the light-off curves for n-butane on ceria and SDC, Fig. 2b), are quite different. The light-off curve for n-butane oxidation over ceria appears to show a transition from one curve to another at approximately 700 K and 35% conversion. At the higher temperatures and conversions, the reaction rates over ceria and SDC are similar. That there appears to be a transition in the rate process with n-butane over ceria, but not with n-butane over SDC, suggests that there is an additional mechanism for n-butane oxidation over ceria that is not important with methane oxidation.

Fig. 3 demonstrates that the two rate processes for n-butane oxidation over ceria are reversible. In this experiment, the n-butane reaction was monitored while ramping the temperature up and down. If the low-temperature process were due to consumption of oxygen that could not be readily replaced from the gas phase, the reaction curve would not be symmetric. This is also an indication that the rates measured during light off represent steady-state rates.

The fact that the low-temperature process on ceria is important for propane and n-butane, but not for methane and ethane, would suggest that methylene ( $-\text{CH}_2-$ ) groups, which are present in propane and n-butane but not in methane and ethane, are involved in that process. Since the methylene C-H bonds are weaker than methyl C-H bonds, it is conceivable that the rate-limiting

step could change from C-H bond scission to ceria re-oxidation. To test for this, we measured light-off curves with the deuterated compounds,  $\text{CD}_4$  and  $\text{C}_4\text{D}_{10}$ , over both ceria and SDC, with results shown in Fig. 4. Fig. 4a) shows that the light-off curves for  $\text{CD}_4$  are shifted to higher temperatures by approximately 40 K compared to the curves for  $\text{CH}_4$  over both ceria and SDC, implying that the oxidation rates for  $\text{CD}_4$  are two to three times lower than those for  $\text{CH}_4$ . The large kinetic-isotope effect demonstrates that the rate-limiting step involves C-H bond scission.

The analogous experiments with n-butane are shown in Fig. 4b). The entire light-off curve is again shifted to higher temperatures with  $\text{C}_4\text{D}_{10}$  compared to  $\text{C}_4\text{H}_{10}$  for both ceria and SDC catalysts; and, as with  $\text{C}_4\text{H}_{10}$ , the oxidation of  $\text{C}_4\text{D}_{10}$  shows the two reaction regimes. While the detailed shape of the light-off curve is affected by the switch to  $\text{C}_4\text{D}_{10}$  (i.e. The conversion at which the transition from one process to the other occurs at a lower value with  $\text{C}_4\text{D}_{10}$ .), it is clear that a similar kinetic-isotope effect is observed for both the low- and high-temperature processes. Therefore, C-H bond scission is involved in the rate-limiting step for both regimes. The magnitude of the shift in the light-off curve for n-butane oxidation is very close to the shift for the methane oxidation.

Based on the observation that both ceria and SDC remain a light yellow color under all of the reaction conditions used in this study [14], significant bulk reduction of either ceria or SDC can be ruled out. However, the oxidation of hydrocarbons over ceria-based oxides almost certainly involves oxidation and reduction of ceria and SDC, at least at the surface. Therefore, we examined the reaction as a function of  $\text{O}_2$  partial pressure to gain insights into the state of the surface under reaction conditions. Fig. 5a) shows the light-off curves for ceria using 15 torr of n-butane and oxygen partial pressures of 101 torr and 180 torr. The data at higher  $\text{O}_2$  pressures is shifted to lower temperatures by almost 20 K, indicating a positive reaction order in  $\text{O}_2$ . The results for the analogous experiment using SDC are shown in Fig. 5b). Since the rates remain unchanged at the higher  $\text{O}_2$  pressure, the reaction on SDC must be nearly zeroth order. This difference in the  $\text{O}_2$  reaction order is also shown in Fig. 5c, which plots the differential rates for n-butane oxidation at 613 K and 13 torr n-butane as a function of  $\text{O}_2$  partial pressure for the ceria and SDC catalysts. The reaction on ceria is approximately half-order, consistent with the 20 K shift in the light-off curve, while the reaction order on SDC is less than 0.1.

To determine the amount of oxygen that is likely involved in the oxidation of n-butane, we performed pulse-reactor measurements using alternate pulses of either 35 torr n-butane or 55



torr O<sub>2</sub> as a function of temperature over both the ceria and SDC samples. In these measurements, a 300-s "pulse" corresponds to approximately 1.0 mmol n-butane per gram of catalyst and 1.6 mmol of O<sub>2</sub> per gram of catalyst. Representative data are shown for ceria at 523 K and 773 K in Fig. 6. There is essentially no reaction at 523 K under steady-state conditions and the pulse data in Fig. 6a) are consistent with this. Fig. 6b) shows that the steady-state rates are high at 773 K; however, even at this temperature, Fig. 6b) shows that only a very small fraction of either the n-butane or O<sub>2</sub> pulses are consumed. All of the CO<sub>2</sub> that forms evolves at the leading edge of the O<sub>2</sub> pulse. In previous studies, it was shown that such rapid evolution of CO<sub>2</sub> is associated with decomposition of carbonates upon oxidation of Ce<sup>+3</sup> to Ce<sup>+4</sup> [16]. That this is indeed the case was confirmed by the infrared measurements shown in Fig. 7. After pulsing the sample with n-butane at 723 K, Fig. 7a), bands associated with carbonate species can be clearly identified between 1200 and 1600 cm<sup>-1</sup>. Passing O<sub>2</sub> over the sample significantly decreased the intensity of these bands, Fig. 7b). It is noteworthy that features associated with C-H stretching modes are also observed between 2800 and 3000 cm<sup>-1</sup>, indicating that there are hydrocarbon species present in the sample after exposure to n-butane; however, these species were not removed by O<sub>2</sub> at the temperature used here.

The amounts of CO<sub>2</sub> that formed in the n-butane-O<sub>2</sub> pulse measurements have been tabulated in Fig. 8 for both the ceria and SDC catalysts. The similarity between Fig. 8 and the light-off curves in Fig. 2b provide strong evidence that there is a correspondence between the two sets of measurements. The data are also very instructive in providing an explanation for the two reaction regimes. Complete reduction of CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub> by n-butane would produce 1790 μmol of CO<sub>2</sub> per gram of CeO<sub>2</sub>, a value much larger than we observe at even the highest temperature we investigated. However, complete reduction of the first monolayer of CeO<sub>2</sub> by n-butane would produce 100 μmol/g. (This calculation is based on removal of 25% of the oxygen atoms at the surface of the (100) surface by complete oxidation of n-butane to CO<sub>2</sub> and H<sub>2</sub>O for a sample with 61 m<sup>2</sup>/g of surface area.) Fig. 8 shows that approximately 40 μmol/g of CO<sub>2</sub> is formed at the point at which the high-temperature rate process becomes important on the ceria catalyst. This in turn suggests that the low-temperature rate process with n-butane oxidation on the ceria catalyst is associated with surface oxygen, while the second rate process occurs when there is free oxygen exchange with the bulk. With SDC, the low-temperature process does not occur, possibly because sites in the vicinity of Sm<sup>+3</sup> are similar to that of a reduced surface.

## Discussion

While questions about alkane oxidation over ceria and doped ceria remain, some of the differences between  $\text{CeO}_2$  and  $\text{Sm}^{+3}$ -doped ceria (SDC) can be explained based on the experimental results in this paper. First, with n-butane oxidation over ceria, there are two rate processes, one that dominates at low temperatures and one that dominates at higher temperatures; and these two processes appear to be correlated with the availability of bulk oxygen. Second, with n-butane, kinetic-isotope effects demonstrate that the rate-limiting step involves C-H bond breakage. Third, the half-order reaction in  $\text{O}_2$  for n-butane on ceria at low temperatures indicates that the reaction is also dependent on the surface-oxygen coverage (The n-butane- $\text{O}_2$  pulse studies demonstrate that bulk reduction of ceria is insignificant until higher temperatures.).

The half-order, rather than first-order, dependence in  $\text{O}_2$  for n-butane oxidation at low temperatures on ceria suggests that this rate process involves dissociatively adsorbed oxygen. Since desorption of  $\text{O}_2$  from  $\text{CeO}_2$  should be very slow below 1200 K [7], the surface coverage of oxygen is likely established by a balance between oxidation of the surface by  $\text{O}_2$  adsorption and reduction of the surface by n-butane reaction. Because the rate of n-butane oxidation is slow relative to the flux of gas-phase  $\text{O}_2$  to the surface, the sticking coefficient for  $\text{O}_2$  must be relatively low. Unlike an adsorption equilibrium, in which the surface coverage decreases with increasing temperature, an adsorption rate would be expected to increase with temperature. However, at higher temperatures, n-butane oxidation over ceria is zeroth-order in  $\text{O}_2$  and the data suggests that a second rate process dominates. The zeroth-order process is consistent with the idea that oxygen from the bulk of the ceria becomes accessible, which is also consistent with the increased amount of oxygen that is removed in the pulse data.

It is easy to explain why there is no low-temperature rate process with methane and ethane over ceria, similar to what is observed with propane and n-butane. Propane and n-butane are much more reactive due to the methylene C-H bonds; methane and ethane are not activated by pure ceria below the temperature at which bulk oxygen becomes available. Indeed, the upward shift in temperature of the light-off curves observed for  $\text{C}_4\text{D}_{10}$  compared to  $\text{C}_4\text{H}_{10}$  was accompanied by a downward shift in the conversion at which the transition occurred from one process to the next. Oxidation rates for methane and ethane over ceria and SDC are similar because Sm-doping poisons only the low-temperature process.

However, two questions that remain unanswered are as follows: 1) What is the oxidation state of the ceria surface in the high-temperature rate process; and 2) what is the role of  $\text{Sm}^{+3}$  in removing the low-temperature rate process for n-butane oxidation? The addition of  $\text{Sm}^{+3}$  decreases the overall rate for n-butane oxidation by removing the low-temperature rate process, suggesting that the surface of SDC is similar to the “reduced” surface of pure ceria. Viewing  $\text{Sm}^{+3}$  as taking the place of  $\text{Ce}^{+3}$ , it is logical that  $\text{Sm}^{+3}$  doping is equivalent to partially reducing the oxide, especially given that the “dopant” level in these materials amounts to 20 mol%  $\text{Sm}^{+3}$  ions. On the other hand, the fact that bulk oxygen becomes available for reaction at the higher temperatures, and presumably available for re-oxidation of the surface, would suggest that the surface of ceria is completely oxidized at the higher temperatures.

It is revealing that the rates for methane and ethane oxidation over ceria and SDC are so similar. First, because it is energetically favorable to have +3 ions migrate to the surface of the cubic fluorite structure [3], it is possible that SDC could be enriched with  $\text{Sm}^{+3}$  at the surface. However, if the surface of our SDC samples was primarily samaria, the rates for methane and ethane would not have been essentially the same on ceria and SDC [15]. Second,  $\text{Sm}^{+3}$  doping is known to increase the ionic conductivity of ceria, something that would be expected to enhance reaction rates, particularly when the bulk oxygen is involved. The fact that  $\text{Sm}^{+3}$  doping does not enhance rates for a process in which bulk oxygen appears to be important is of interest.

Assuming our interpretation is correct, it is noteworthy that oxygen exchange between the surface and the bulk of ceria begins at approximately 650 K. This suggests that reactions at lower temperatures involve oxidation and reduction of only the surface ceria, which in turn has important consequences for the design of catalysts that will operate at lower temperatures, such as those for the water-gas-shift reaction [16, 17]. Those catalysts will also contain precious metals that will promote reduction of the surface ceria, but bulk ceria would not be expected to play an important role.

Finally, on a practical point, the fact that methane oxidation occurs at almost exactly the same rate over ceria and SDC, while n-butane oxidation occurs at dramatically different rates over these two materials, has important implications for how one characterizes materials. For example, it is common practice to use temperature-programmed reduction with  $\text{H}_2$  to determine the relative reactivity of a series of catalysts. The underlying assumption is that the oxidation reaction of interest will scale with the rate of  $\text{H}_2$  oxidation. Obviously, if the rate of methane

oxidation does not scale with the rate of n-butane oxidation, one should be cautious in assuming that other reactions will scale with H<sub>2</sub> oxidation.

### Conclusions

Sm<sup>+3</sup> doping of ceria affects oxidation of propane and n-butane dramatically while have no effect at all over methane and ethane oxidation. The difference with reactants is due to the fact that there is a low-temperature rate process with n-butane oxidation over ceria, not observed with methane, that is removed by doping with Sm. The results indicate that a common assumption, that doping ceria should increase its reactivity, is not generally correct. Also, the assumption that a catalyst which exhibits higher activity for one oxidation reaction will also show higher reactivities for other hydrocarbon reactions is not always valid.

### Acknowledgements

This work was supported by the DOE, Basic Energy Sciences, Grant #DE-FG03-85-13350.

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**Table 1. Differential Rates and Activation Energies for the Hydrocarbon Oxidation Reaction on Ceria and SDC**

Reaction	Catalyst	Rate at 693 K (molecules/(s.m <sup>2</sup> ))	Activation Energy (± 5 kJ/mol) <sup>b</sup>
Methane	Ceria	4.2 x 10 <sup>15</sup>	115
Oxidation	SDC	3.9 x 10 <sup>15</sup>	120
Ethane	Ceria	1.0 x 10 <sup>16</sup>	120
Oxidation	SDC	1.0 x 10 <sup>16</sup>	125
Propane	Ceria	1.4 x 10 <sup>17a</sup>	70
Oxidation	SDC	1.3 x 10 <sup>16</sup>	125
n-Butane	Ceria	3.5 x 10 <sup>18a</sup>	105
Oxidation	SDC	7.8 x 10 <sup>15</sup>	105

a. The data are extrapolated from the Arrhenius plots.

b. The activation energy is calculated using Arrhenius equation.

## Figure Captions

Fig. 1 The differential reaction rates of hydrocarbon oxidation on ceria ( $\blacktriangle$ ) and SDC ( $\square$ ) under (a) 109 torr  $\text{CH}_4$  and 217 torr  $\text{O}_2$ ; (b) 31 torr  $\text{C}_2\text{H}_6$  and 109 torr  $\text{O}_2$ ; (c) 25 torr  $\text{C}_3\text{H}_8$  and 125 torr  $\text{O}_2$ ; and (d) 17 torr n- $\text{C}_4\text{H}_{10}$  and 111 torr  $\text{O}_2$ .

Fig. 2 The hydrocarbon oxidation light-off curves over ceria (solid line) and SDC (dotted line). (a) 109 torr  $\text{CH}_4$  and 217 torr  $\text{O}_2$  and (b) 17 torr n- $\text{C}_4\text{H}_{10}$  and 111 torr  $\text{O}_2$ ;

Fig. 3 The butane oxidation light-off and light-down curves over ceria. The ratio of butane to oxygen is 1:6.5. The temperature was programmed at the following steps. (a) The temperature was ramping from 298 K to 873 K linearly in 58 mins. (b) The temperature was kept at 873 K for 5 mins. (c) The temperature was cooling down from 873 K to 298 K linearly in 58 mins.

Fig. 4. Plots of the isotopic studies on ceria.

(a) Methane ( $\text{CH}_4$ ) and deuterated methane ( $\text{CD}_4$ ) conversion is plotted as a function of temperature under the partial pressure of 109 torr fuel and 217 torr oxygen.

(b) Butane ( $\text{C}_4\text{H}_{10}$ ) and deuterated butane ( $\text{C}_4\text{D}_{10}$ ) conversion is plotted as a function of temperature under the partial pressure of 17 torr fuel and 111 torr oxygen.

—  $\text{C}_4\text{H}_{10}$  on ceria  
 - -  $\text{C}_4\text{H}_{10}$  on SDC  
 — $\triangle$ —  $\text{C}_4\text{D}_{10}$  on ceria  
 — $\square$ —  $\text{C}_4\text{D}_{10}$  on SDC

Fig. 5. Plots of pressure-dependence for the n-butane oxidation on ceria and SDC. (a) Butane oxidation light-off measurements on ceria. The partial pressure of n-butane is fixed at 15 torr. The partial pressure of oxygen is 101 torr (I) and 181 torr (II). (b) Butane oxidation light-off measurements on SDC. The partial pressure of n-butane is fixed at 15 torr. The partial pressure of oxygen is 101 torr (I) and 181 torr (II). (c) Differential reaction rates as

a function of oxygen partial pressure for the n-butane partial pressure of 13 torr and a temperature of 613 K over ceria (I) and SDC (II).

Fig. 6 n-Butane-oxygen pulse measurements on ceria at (a) 523K and (b) 773 K. The data are for two pulses of n-C<sub>4</sub>H<sub>10</sub> ( $m/e = 43$ ), followed by two pulses of O<sub>2</sub> ( $m/e = 32$ ) and another n-C<sub>4</sub>H<sub>10</sub>. The partial pressures of the n-C<sub>4</sub>H<sub>10</sub> and O<sub>2</sub> were 35 torr and 55 torr respectively. Formation of CO<sub>2</sub> ( $m/e = 44$  and 28) and CO ( $m/e = 28$ ) is observed in the pulses.

Fig. 7. Diffuse reflectance FTIR spectra for ceria at 723K. (a) oxidized sample exposed to 25 torr butane, followed by flushing in He; (b) sample exposed to 50 torr oxygen, then flushed in He.

Fig. 8. The CO<sub>2</sub> production in the n-butane-oxygen (n-butane pressure was 35 torr and oxygen pressure 55 torr.) pulses shown as a function of temperature.

(▲) Ceria

(□) SDC.

Figure1a

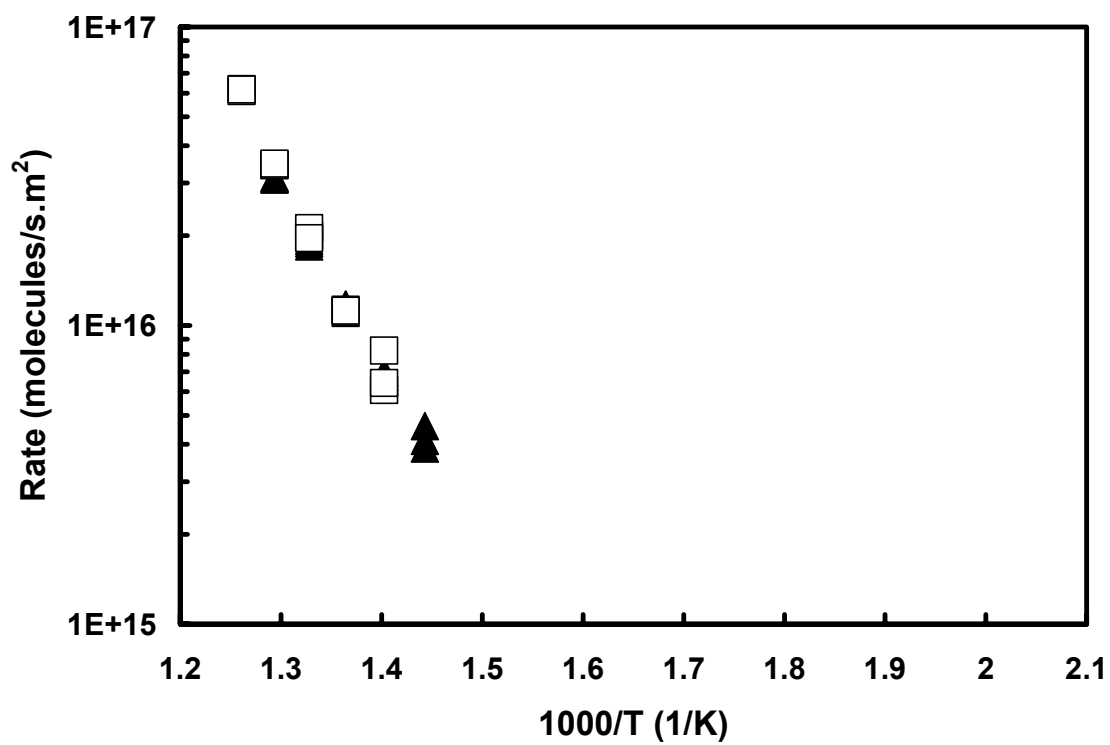


Figure1b

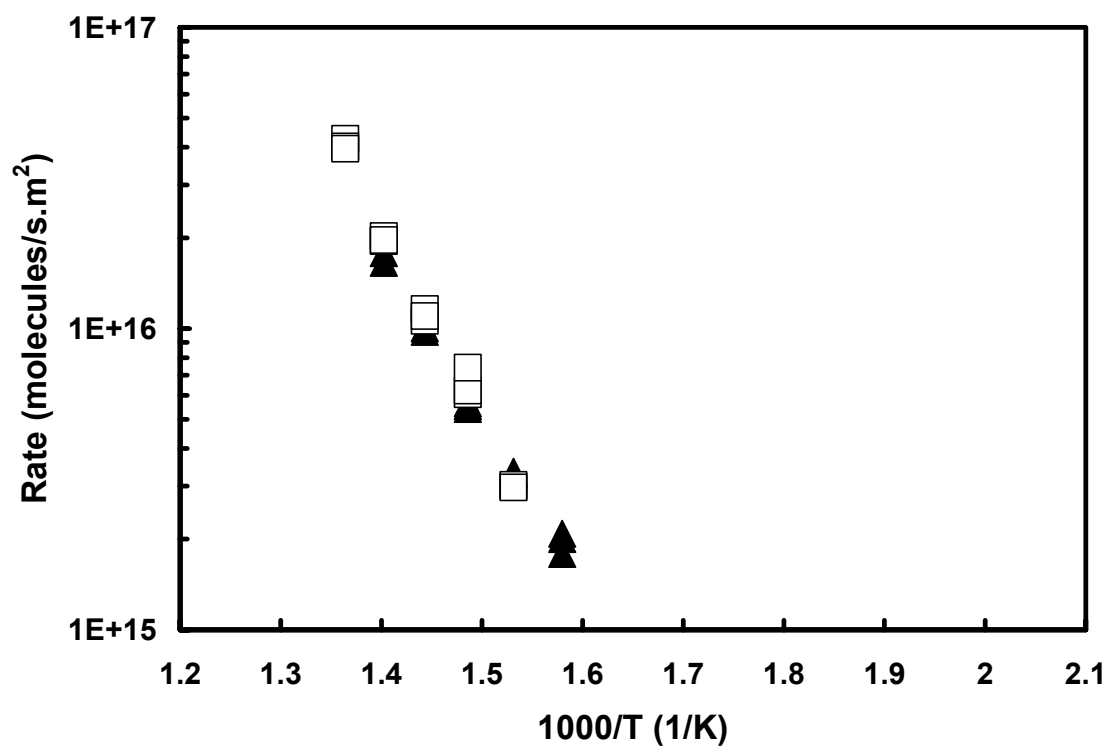




Figure 1c

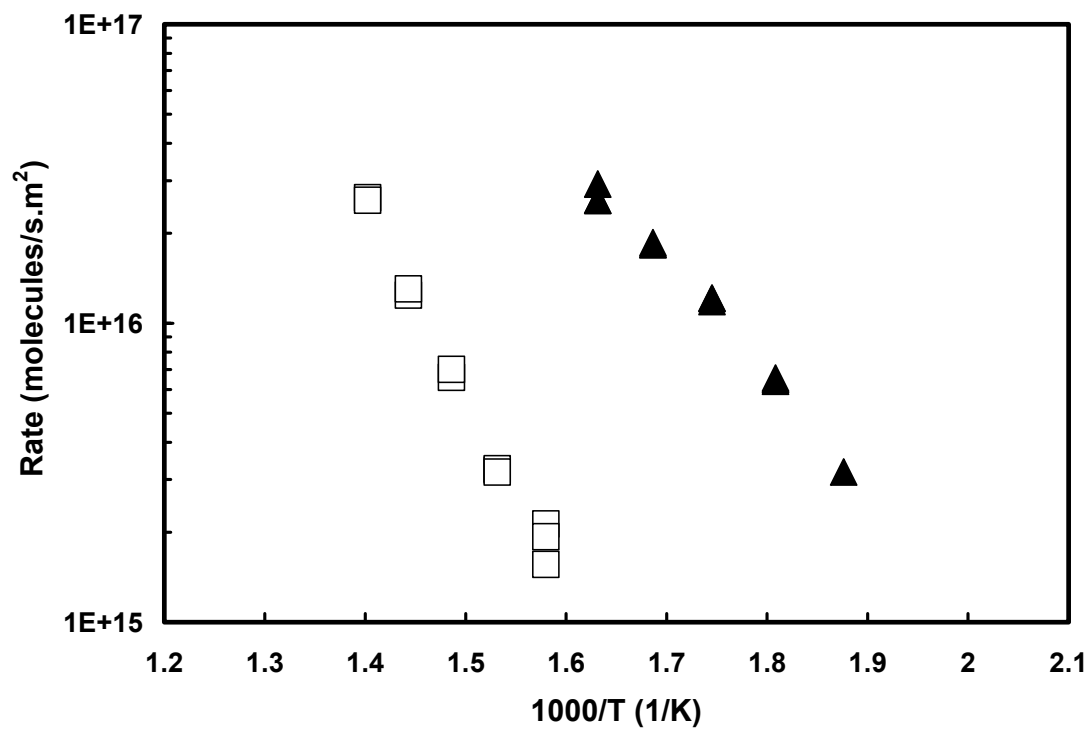


Figure 1d

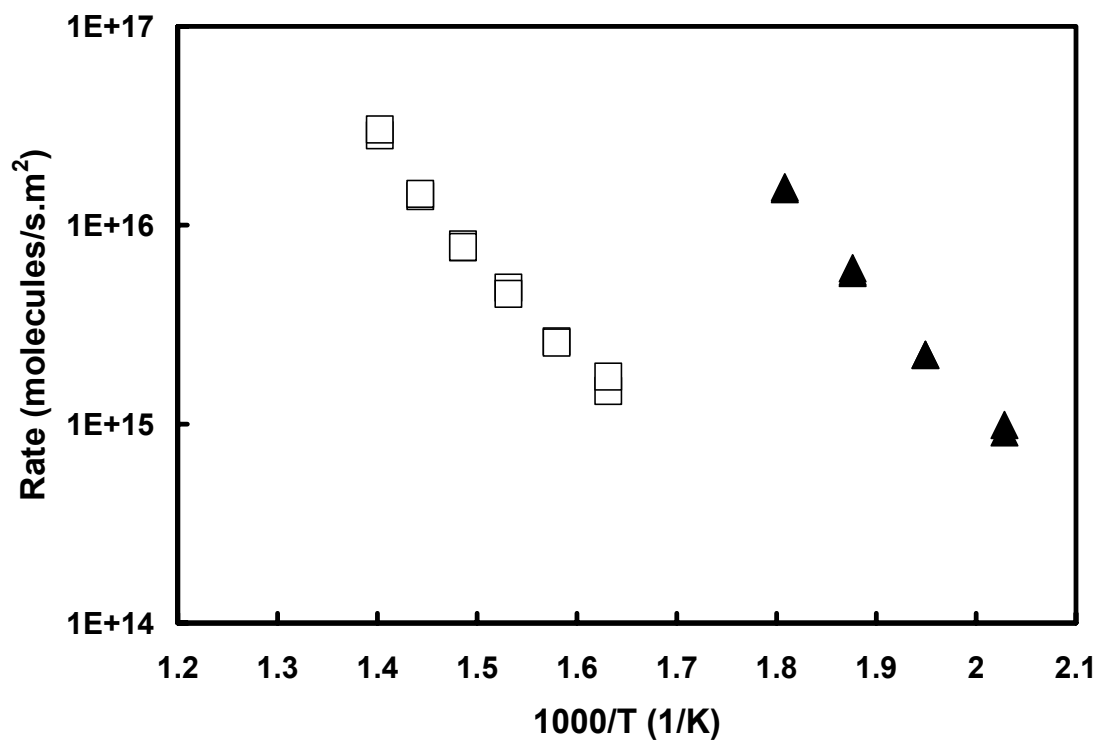


Figure 2a

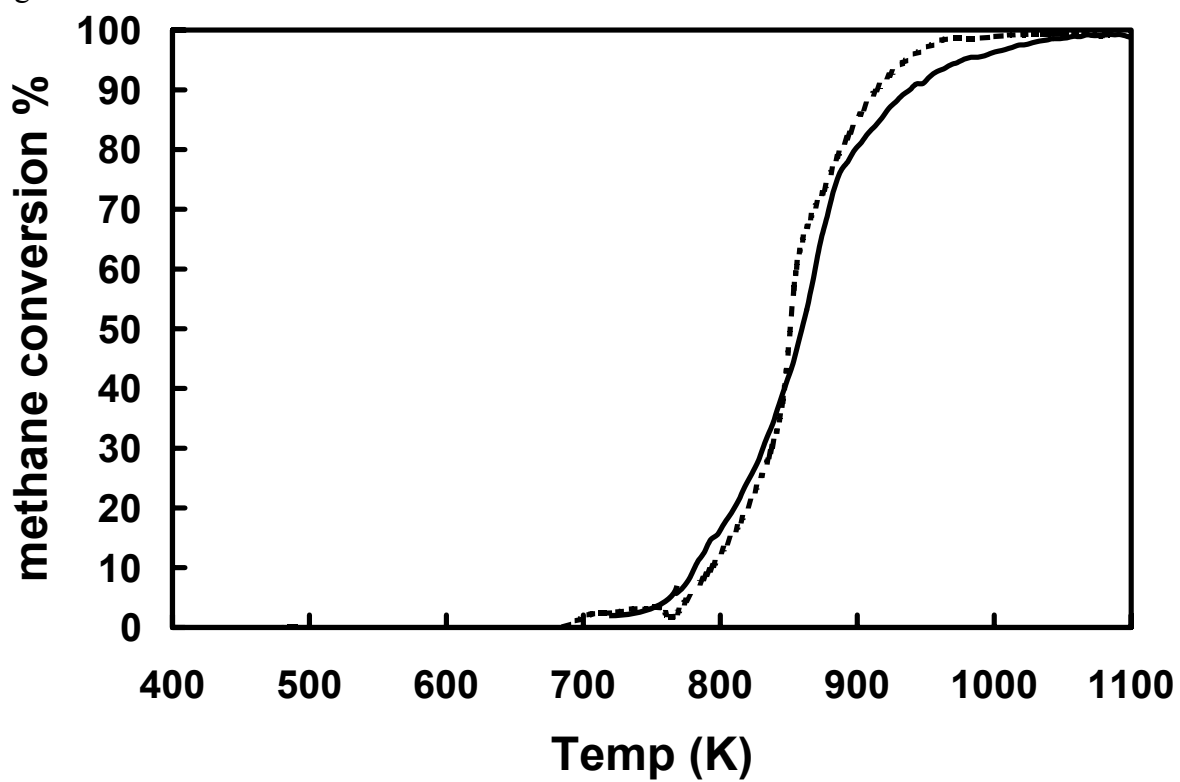


Figure 2b

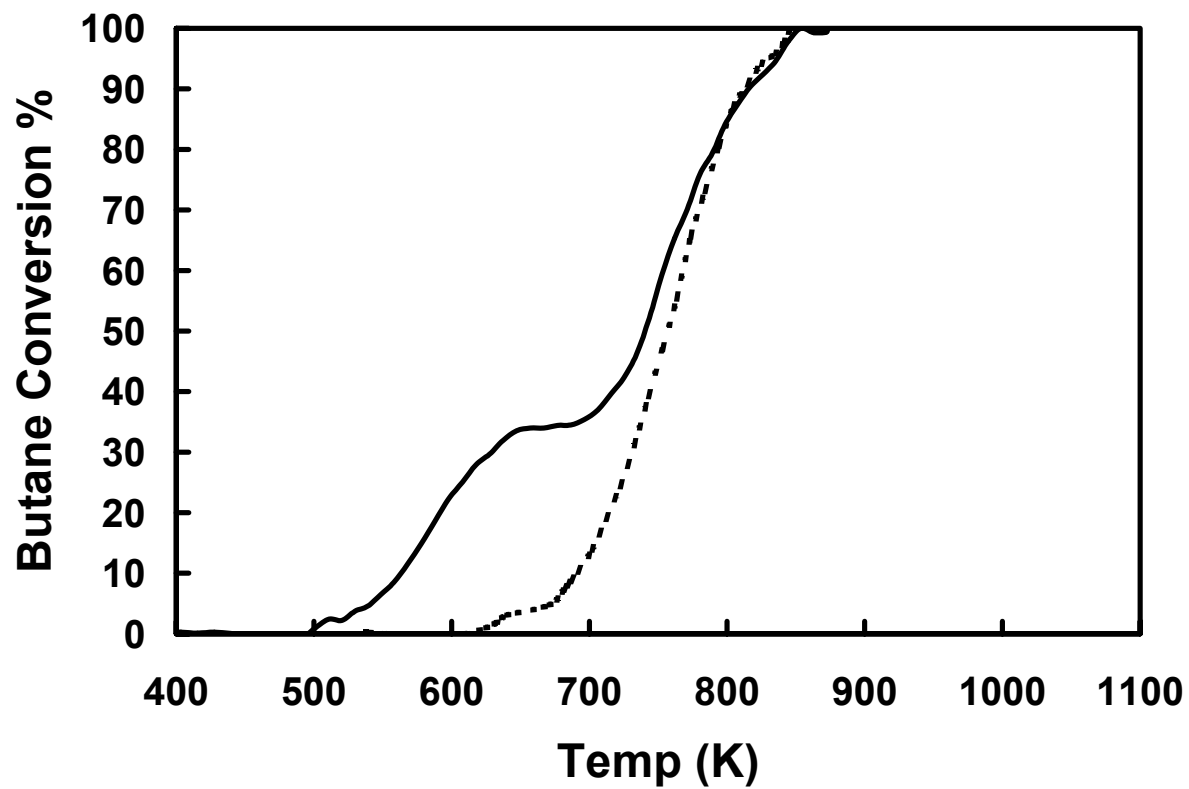


Figure 3

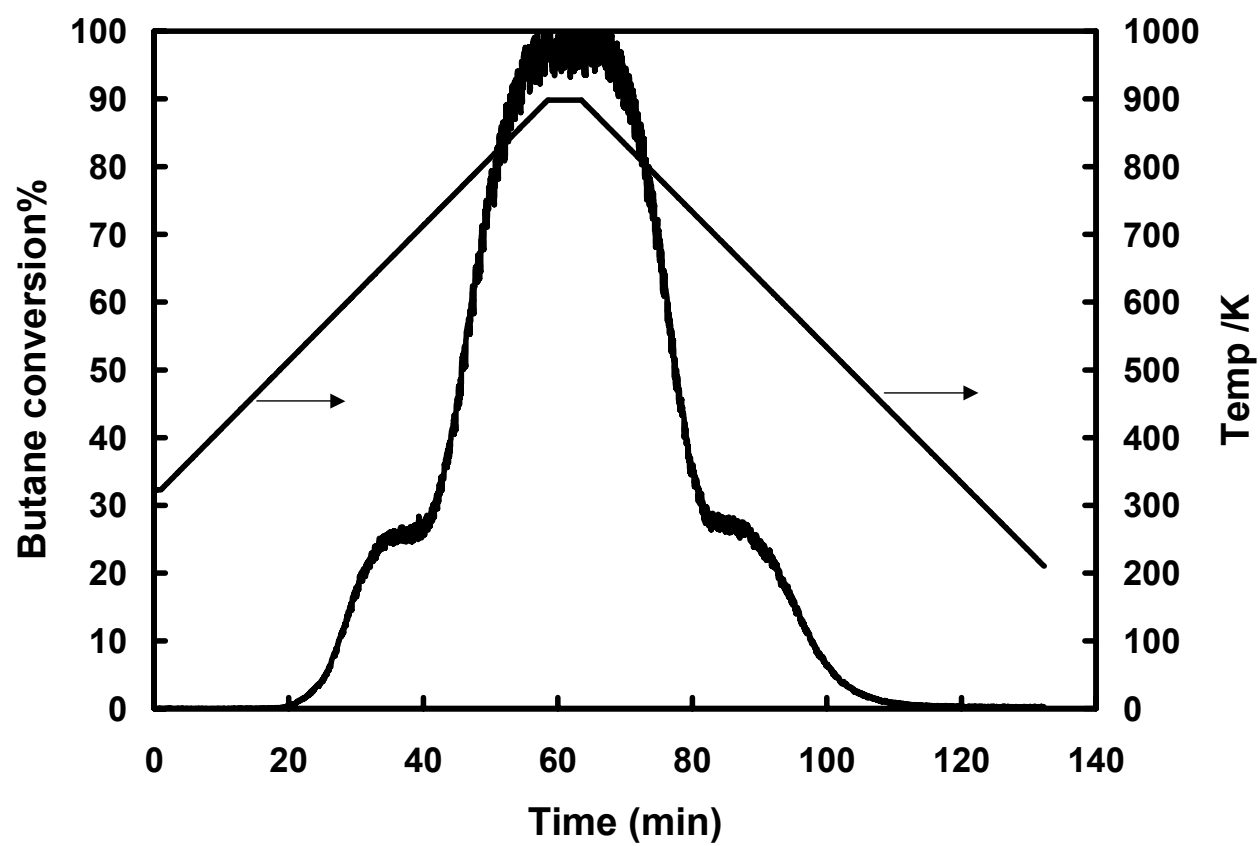


Figure 4a

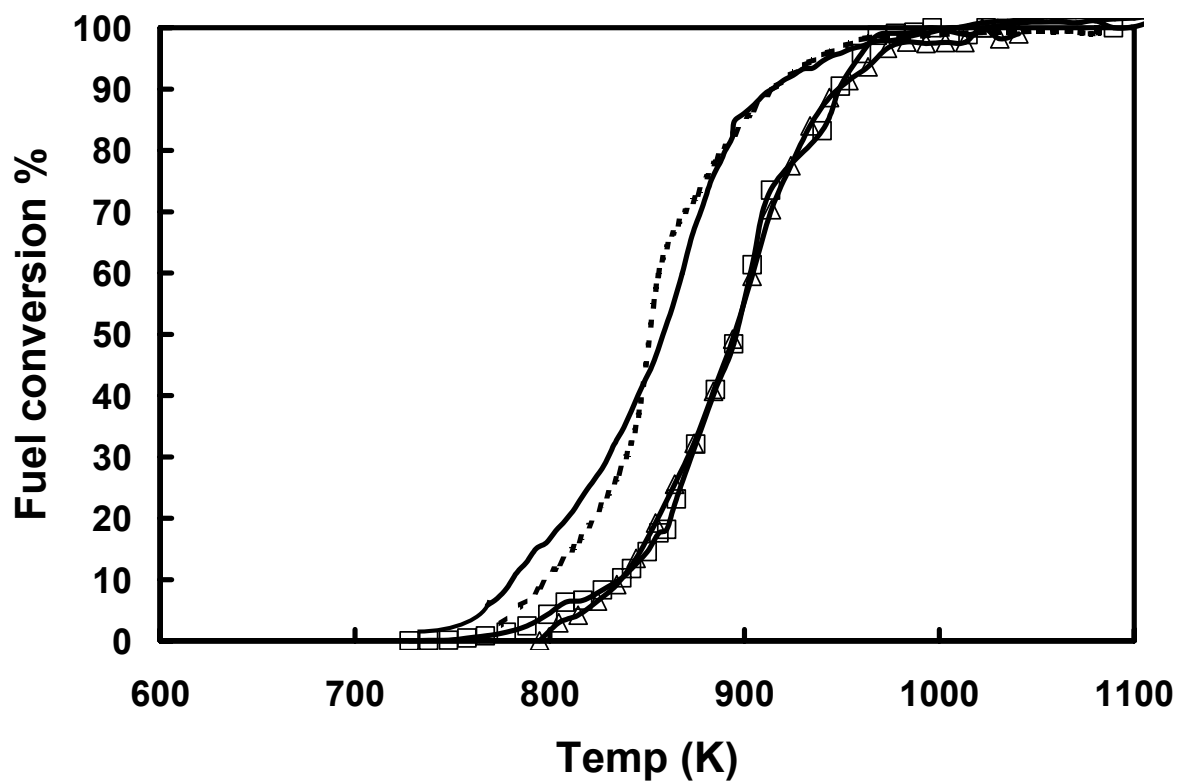


Figure 4b

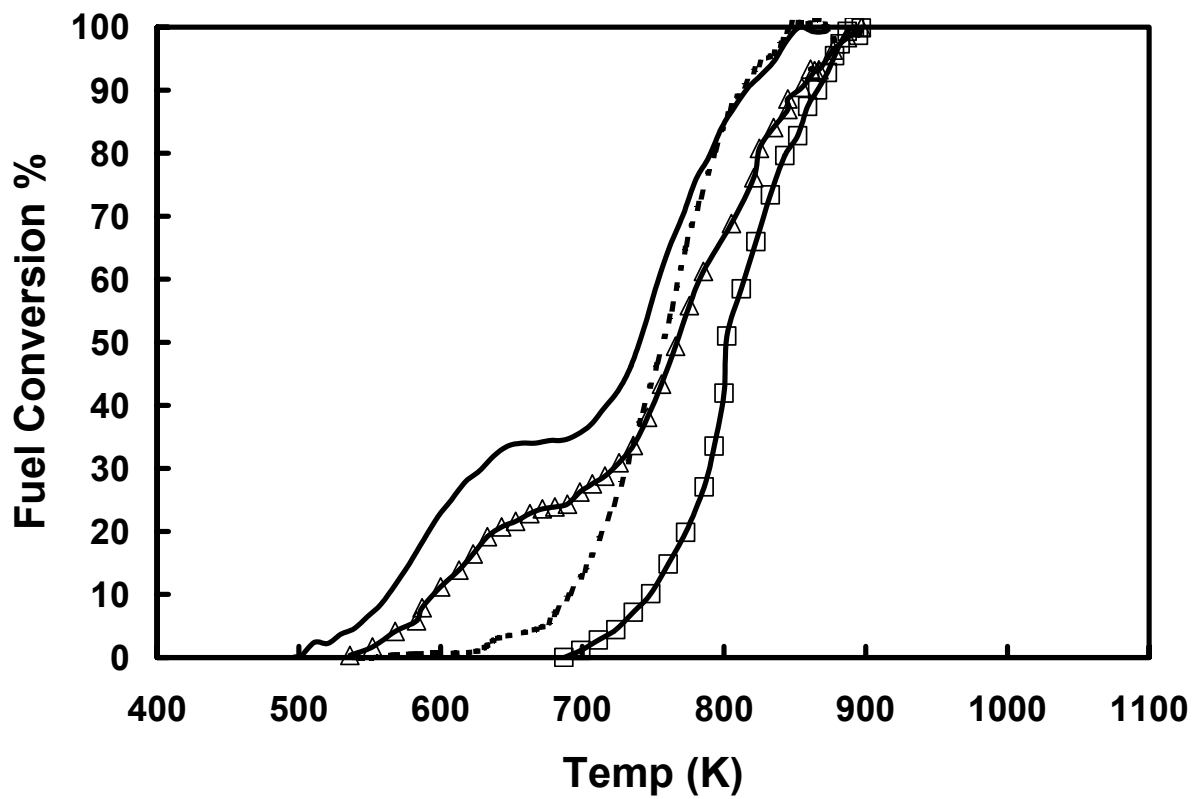


Figure 5a

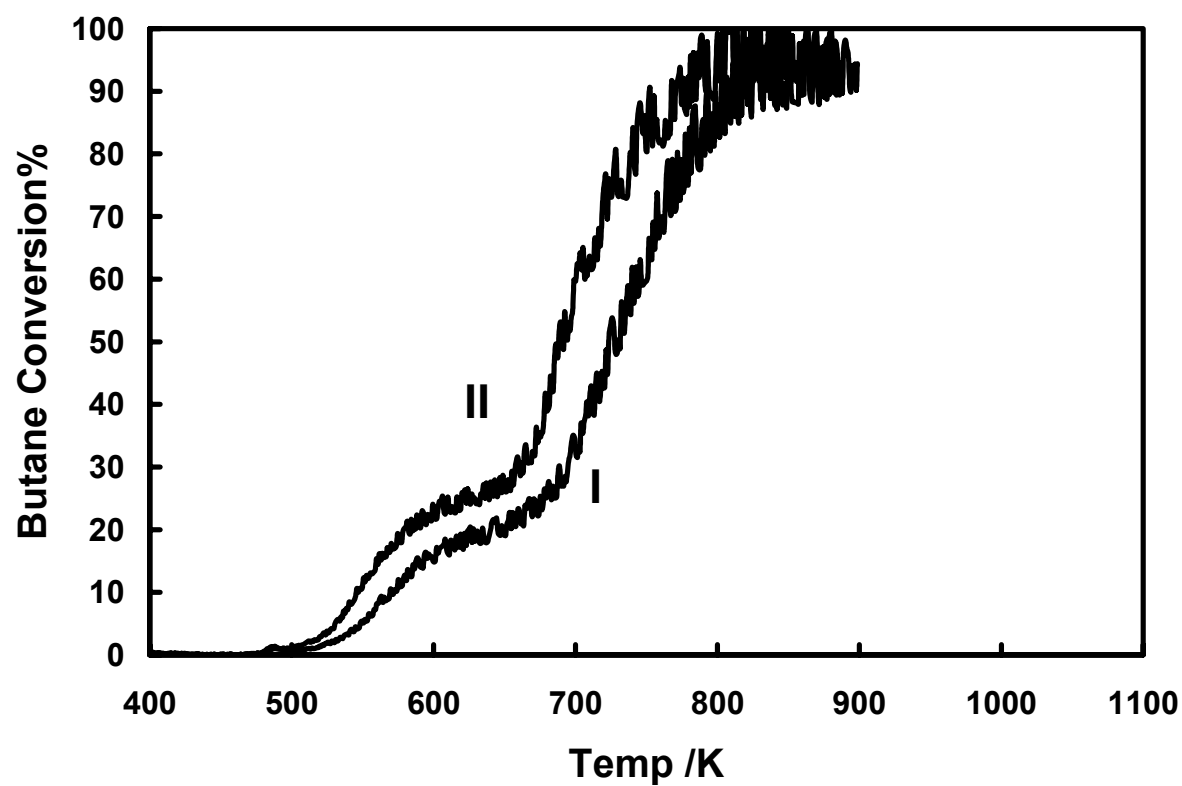


Figure 5b

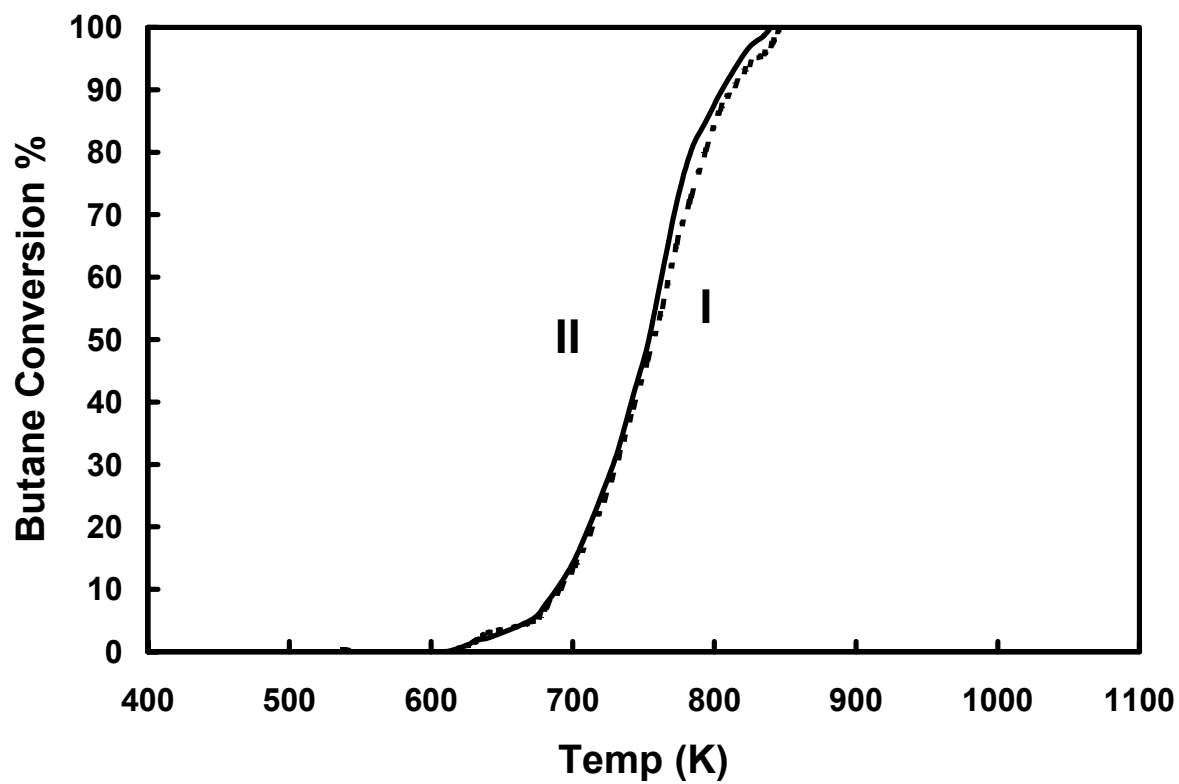


Figure 5c

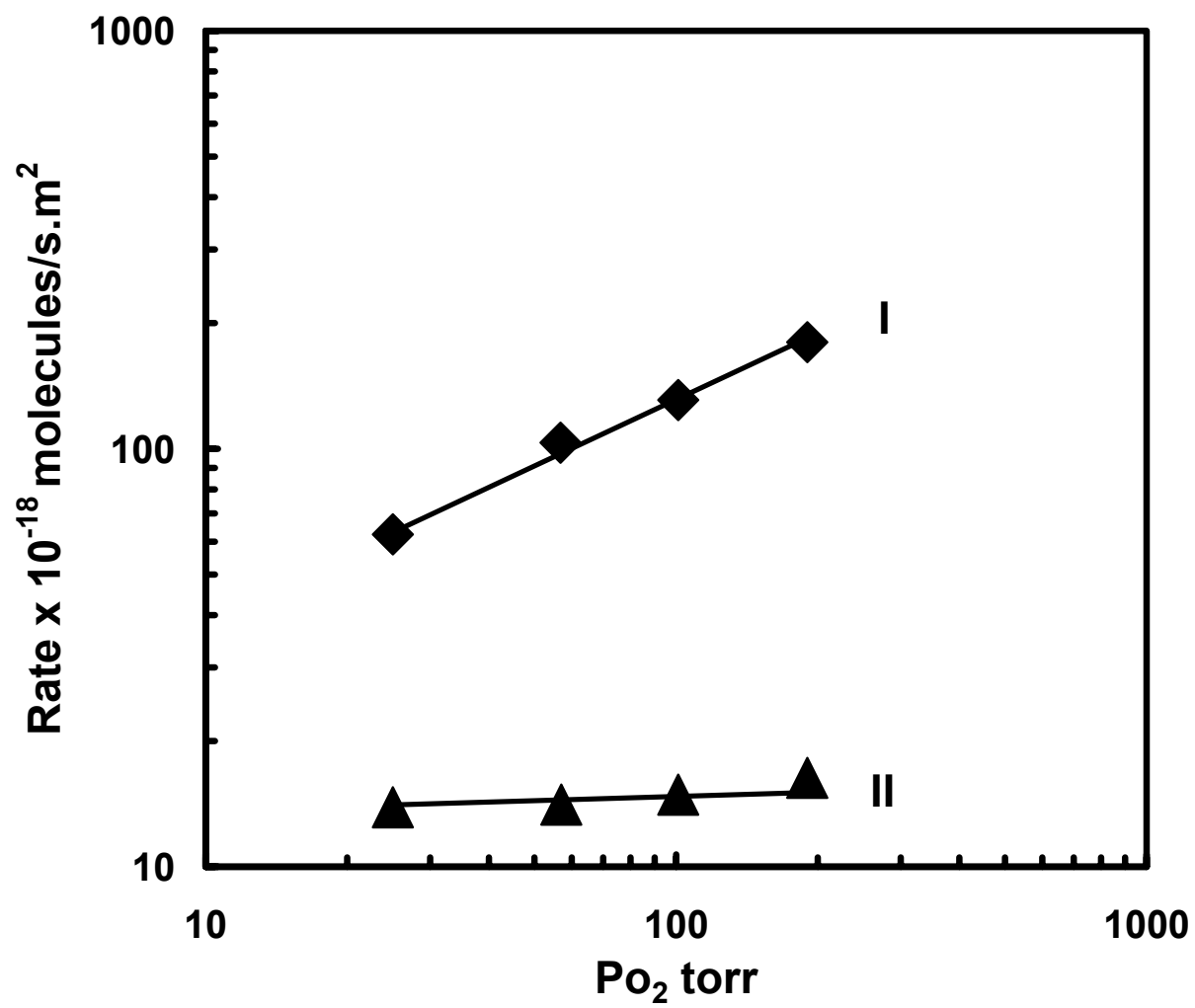




Figure 6a

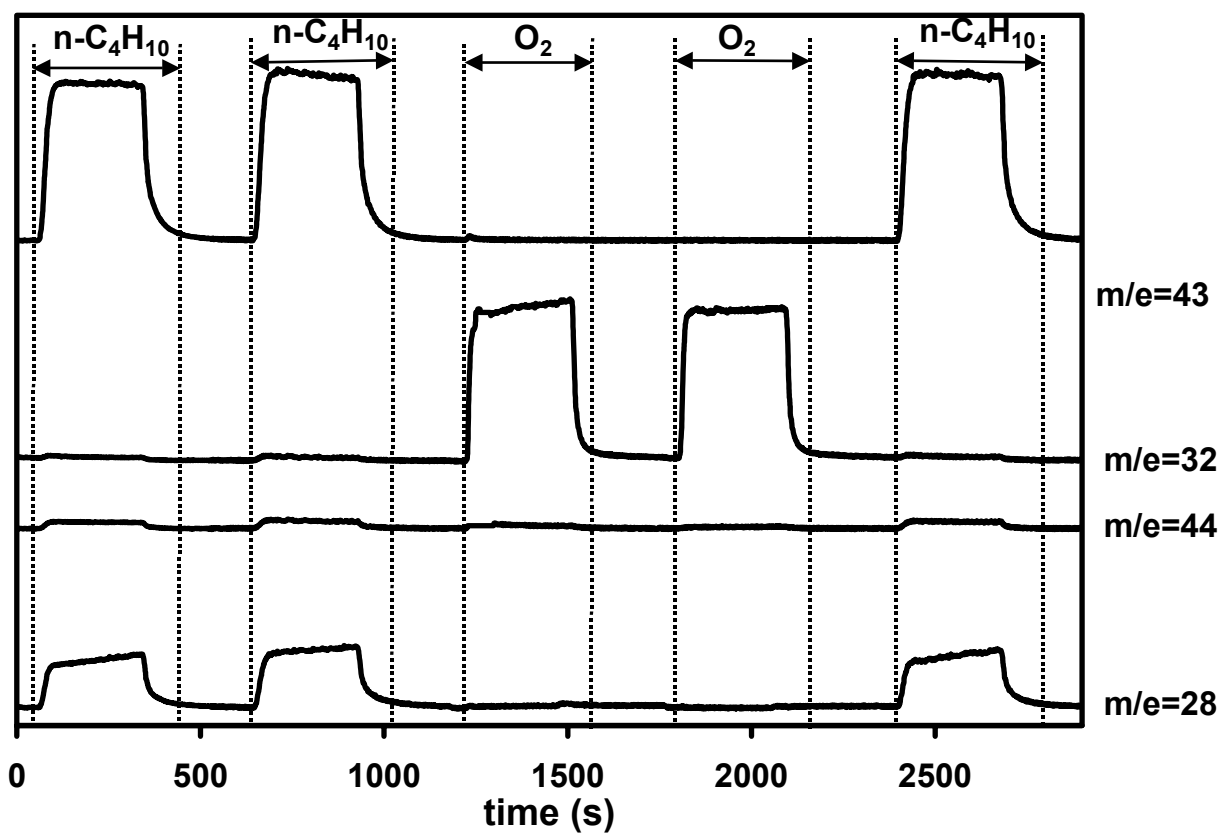


Figure 6b

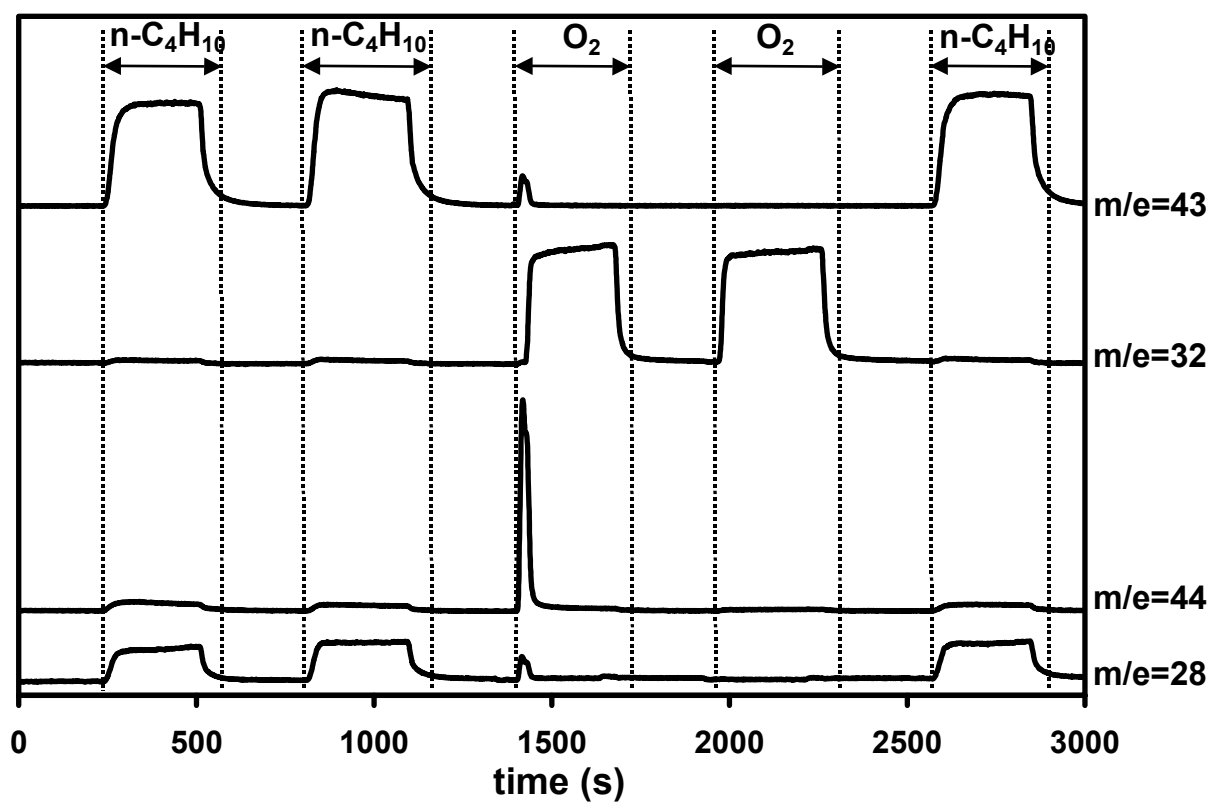




Figure 7

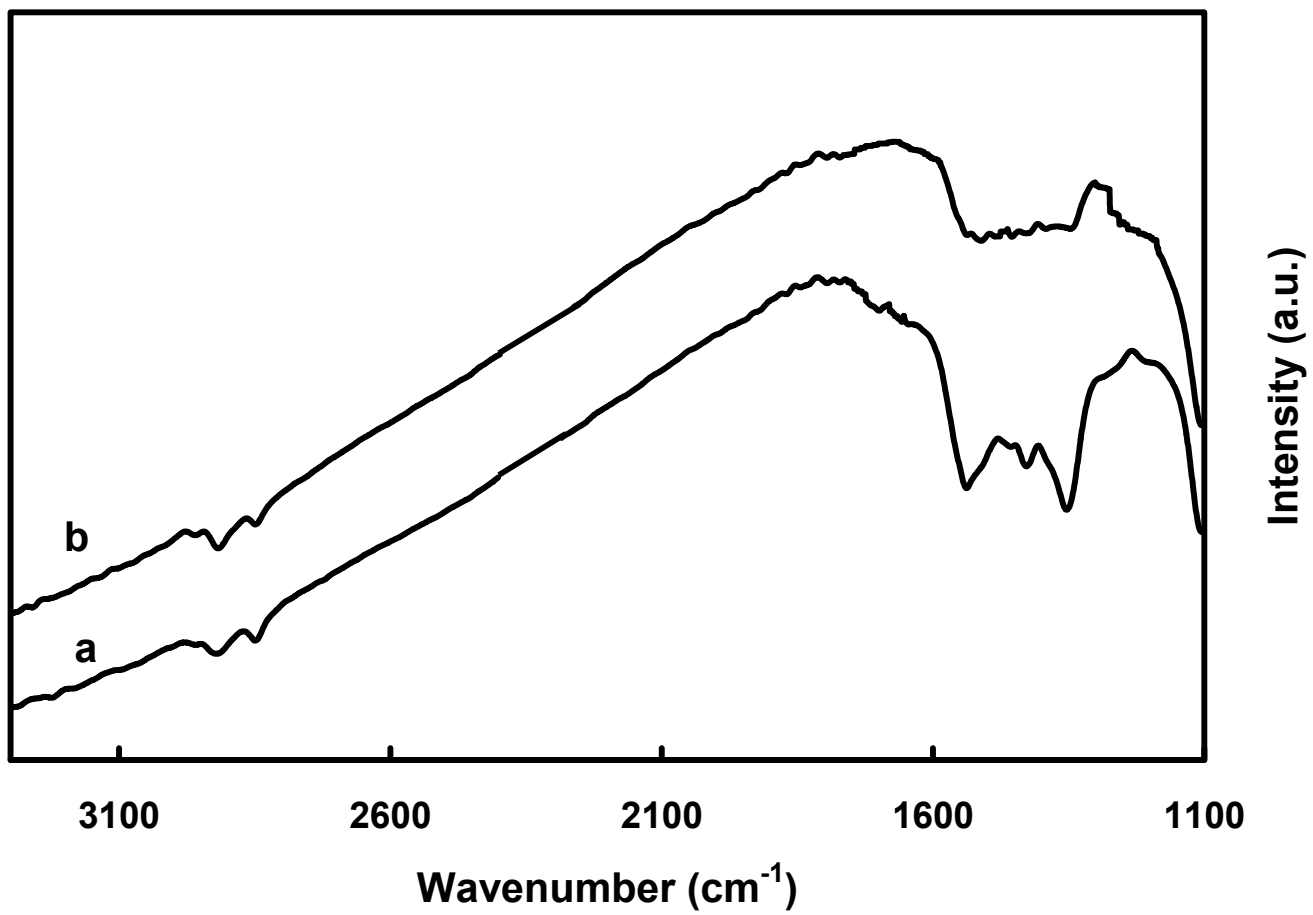


Figure 8

