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Partial Oxidation of Propane with CO₂ on Ru doped Catalysts

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Abstract

The catalytic activity and stability of Ru doped CeO₂ and Ru doped ZrO₂ are investigated and compared for the partial oxidation of propane using carbon dioxide as an oxidant. On both the reducible Ru doped ceria and the irreducible Ru doped zirconia catalysts, the major products of propane partial oxidation were CO and H₂ when CO₂ is used as an oxidant, and the two catalysts had comparable activity below 450 °C. In addition to dry reforming products, the Ru doped CeO₂ produced small quantities of methane above 450 °C. Neither catalyst showed measurable selectivity for oxidative dehydrogenation activity of propane-to-propylene with CO₂ or CO. Coke formation will limit the utility of either catalyst for dry reforming of propane in practice.

1. Introduction

The utilization of carbon dioxide as a reactant in chemical conversions is of fundamental and practical interest. One use of carbon dioxide is as an oxygen source or oxidant in partial oxidation reactions of alkanes and oxidative dehydrogenation (ODH) of propane, isobutane and ethylbenzene¹⁻⁶. Dry reforming of light alkanes can be used to produce synthesis gas. Use of abundant propane is a potential feedstock for producing synthesis gas:

Synthesis gas is commercially generated by several processes including: hydrocarbon reforming⁷⁻⁹ and occasional reforming of alcohols¹⁰⁻¹³. Gasification of coal or biomass in limited oxygen is also utilized^{14,17}. Reforming of propane with carbon dioxide (Eq. (1)) has been proposed as a pathway for synthesis gas and/or hydrogen production using abundant propane; a major constituent of liquefied petroleum gas (LPG) now produced from low-cost shale gas¹⁸⁻¹⁹. Reforming of hydrocarbons and alcohols primarily yields a mixture of hydrogen, and CO, including CO₂ and H₂O as minor constituents. The hydrogen produced can be either separated, or utilized with CO as synthesis gas for the downstream production of a number of fuels and chemicals including methanol, ammonia, olefins, and liquid fuels²⁰⁻²³.

If syngas or hydrogen is desirable final products, then it is important that to prevent further reactions of hydrogen including methanation:

Several catalysts have been reported for propane reforming, including nickel based²⁴⁻²⁶ and noble metal based catalysts^{9, 18-19, 27-30} (Pt, Rh, Pd, etc.). Olsbye et al. reported²¹⁻²³ an exceptionally stable Ni/Mg(Al)O hydrotalcite catalyst for propane dry reforming. The high activity of the catalysts depends strongly on the Ni particle size. Mechanistic studies have shown C-C bond rupture is the rate determining step²⁶. Investigating a bimetallic Co-Ni/Al₂O₃ catalyst in both dry reforming (DR) and steam reforming (SR) of propane, it was reported that carbon deposition was the main cause of catalyst deactivation^{26, 31}. In the case of SR, separate studies on the effects of preparation method and lanthanide elements on propane SR performance of Ni-Al₂O₃ catalysts were reported³²⁻³³. By adding small amounts (2 wt %) of lanthanide elements (i.e., La, Ce, and Yb) significantly improves steam reforming activity and stability. However the catalyst deactivates faster at high reaction temperature and the activity loss was suppressed by increasing H₂O/C ratio. The catalyst deactivation is due to nickel sintering and coke formation. Studies of oxidative steam reforming (OSR) of propane, Rh/Al₂O₃^{9, 19}, Ce_{1-x} Ni_xO₂¹⁸ and Pd/CeO₂/Al₂O₃³⁰ were investigated by different groups. CeO₂ and Al₂O₃ supported Pd catalyst mainly produces higher yield of hydrogen and high H₂/CO ratio by promoting water gas shift reaction. Methanation and propane cracking was not observed during the reaction. Higher yield of hydrogen observed on supported Rh/Al₂O₃ catalyst. At shorter residence time higher amounts of hydrocarbon byproducts observed, however complete hydrocarbon oxidation noticed at longer residence time producing CO₂ and H₂O.

There have been few reports of partial oxidation of propane with CO₂ as an oxidant. Sutton et al.³⁴ examined the kinetics and the mechanism of propane partial oxidation over Ru supported on Al₂O₃. This catalyst mainly promotes syngas. The ratio of CO/H₂ increases with increase in temperature. Recently, low temperature oxidation in oxygen of butane³⁵ has been studied over Ru/Al₂O₃ catalysts prepared by the incipient wetness impregnation method using RuCl₃ as a metal precursor. It was found that in the presence of large amount of chlorine on the

catalyst surface, the catalytic activity towards the C₃–C₄ alkanes oxidation were greatly suppressed. Also, the pre-treatment in oxygen at different temperatures (250 °C and 600 °C) induce significant loss of activity of the Ru/Al₂O₃ catalysts in both reactions. The activity loss was attributed to the formation of crystalline RuO₂ oxide and to sintering of the active phase.

We are interested in doped metal oxide catalysts and their reactivity for propane partial oxidation using carbon dioxide as an oxidant. Doped metal oxide catalysts may be more active and stable compared to supported metal oxide catalysts in some instances. In prior work we showed that ceria doped with ruthenium is an active and stable catalyst for carbon dioxide methanation³⁷. In this paper we examine the hypothesis that doping metal oxides relatively inactive metal oxides with Ru would promote partial oxidation of propane and that the hydrogen produced during dehydrogenation would react with carbon dioxide to produce methane (equation 2) which would be facilitated by the methanation activity of Ru doped ceria. Ceria is redox active metal oxide which when partially reduced contains abundant vacancies making the surface relatively basic and reactive to CO₂ (a Lewis acid) forming carbonate intermediates. Whereas, zirconia is a less reducible oxide generally considered to be an “acidic” metal oxide and not as reactive for acidic CO₂⁴⁵⁻⁴⁶. For both ceria and zirconia we expect that the substitution of an Ru atom as a lower valence dopant for a 4+ cation (Ce or Zr) will make both surfaces more reducible and more able to form surface oxygen vacancies and reactive for CO₂. The surface reaction of propane dehydrogenation can reduce the ceria producing the vacancies needed to create a surface with increased reactivity for CO₂. We are interested in measuring the relative reactivities of the low valence Ru dopant in the two different host oxides. The aim of this work is to study the partial oxidation of propane using CO₂ as an oxidant and to address the following questions:

- 1) What is the activity and selectivity of 5% Ru doped CeO₂ for partial oxidation of propane compare to 5% Ru doped ZrO₂?
- 2) What is the effect of support and oxygen transfer capacity on the progress of partial oxidation?

We examine the catalyst performance over a range of conditions including temperature, feed ratios, and space times.

2. Experimental Methods

Catalyst Synthesis

5% Ru doped CeO₂ and 5% Ru doped ZrO₂ catalysts were synthesized by using the combustion method in our previous work³⁷. The combustion synthesis method was used for both catalyst which has been shown to dope catalysts; our group has studied Ru doped CeO₂ and synchrotron XRD and activity studies suggest an single phase doped oxide material using this method. In a typical preparation, 2.5g of ceric ammonium nitrate, 49.78 mg of RuCl₃, and 1.25 g of oxalic dihydrazide are dissolved in distilled water. Similarly, for synthesis of Ru doped ZrO₂, 2.5g of zirconyl nitrate (ZrO(NO₃)₂·6H₂O), 80 mg of RuCl₃, and 1.39 g of oxalic dihydrazide are dissolved in distilled water. The aqueous mixture is put into a muffle furnace at 550 °C until combustion occurs spontaneously giving the final Ce_{0.95} Ru_{0.05}O₂ and Zr_{0.95} Ru_{0.05}O₂ product.

Catalyst Characterization

To determine whether or not a “doped” oxide was indeed created or if the Ru created separate phases, XRD powder diffraction was used (Philips XPERT MPD, Cu K_α) and the reflections between 10 and 90 degrees.

BET surface areas were measured by N₂ physisorption at -196 °C using Tristar 3000 Gas Absorption Analyzer, Micromeritics). Samples were out-gased at 120 °C under a flow of N₂ for 12 h prior to analysis.

The morphology of the doped samples was characterized by scanning electron microscopy (FEI XL30 Sirion FEG Digital microscopy). Transmission electron microscopy (TEM) images of the powder samples were recorded on a FEI Tecnai G2 Sphera Microscope.

Oxygen storage capacity (OSC) measurements were carried out in a plug flow reactor coupled to a mass spectrometer. Before performing the oxygen storage capacity, the catalyst was heated in the flow of Ar at 500 °C for an hour to remove adsorbed water and residual water in the reactor from the surface. Then the samples were reduced under H₂ (30% H₂ in Ar) at 500 °C for 1 h. Then, the samples were cooled to 450 °C and purged in Ar at 450 °C. O₂ was injected to the catalyst surface until the oxygen uptake was finished. Integration of the partial pressure as a

function of time was used to accurately determine the amounts of O₂ consumed during the O₂ step pulses. The amount of oxygen consumed on the catalysts was calculated by subtracting the unreacted O₂ from the blank O₂ injected at room temperature.

The H₂-TPR was performed in a plug flow reactor coupled to a mass spectrometer. Before performing TPR, the catalyst was pretreated at 500 °C with heating rate of 10 °C/min, followed by cooling in Ar flow to room temperature. Then the H₂-TPR reaction was carried out from room temperature to 550 °C. The H₂ uptake was detected by mass spectrometer by change in partial pressure of H₂. The maximum amount of hydrogen consumed correlates the maximum amount of water produced. By integrating the partial pressure of H₂O as a function of time was used to accurately determine the amounts of H₂O produced during the H₂-TPR. To quantify H₂ uptake⁴⁴, the number of moles of oxygen was subtracted from the total mole of H₂O produced.

In order to investigate the coke after propane dry reforming, the temperature was cooled to 25 °C then propane & CO₂ was switched off from the gas stream. Temperature programmed oxidation was carried out by introducing 10% oxygen through the catalyst bed to oxidize the carbon deposited on the catalyst surface. The CO₂ formed during carbon burning was quantified by integrating the area under the peak. Prior to CO₂ quantification the mass spectrometer was calibrated by injecting the known amount of CO₂. The number of CO₂ formed is converted into carbon and then calculated the carbon deposition per gram of the catalyst.

Catalyst Testing

The catalysts were tested for partial oxidation of propane using the quartz reactor with inner diameters of 3.75 mm and length 300 mm fitted inside a stainless steel heating block in the temperature range of 200-550 °C and at atmospheric pressure. 25 mg of the catalyst used with 50 mg of SiO₂ (Chromatographic grade, mesh 200) as diluents. The diluent SiO₂ is very inert and show no catalytic activity. Process gases (Ar, propane and CO₂) were individually connected and controlled by mass flow controllers (MKS). The product gas stream was sampled directly at the reactor outlet with a differentially pumped mass spectrometer (Stanford Research Systems RGA 200) through a controlled leak valve. For temperature-programmed reaction (TPR) studies, the temperature was ramped at the rate of 10 °C min⁻¹ using a programmable temperature controller (Omega, CSC32).

3. Results and Discussion

Catalyst Structure

Figure 1 shows XRD results obtained from the freshly prepared catalysts after calcinations at 550 °C. Diffraction peaks (Figure 1a) for both the CeO₂ and 5% Ru doped CeO₂ show the fluorite structure. The XRD data from ZrO₂ and 5% Ru doped ZrO₂ showed in Figure 1 (b). Pure ZrO₂ showed characteristic diffraction peaks corresponding to monoclinic (m-ZrO₂) and tetragonal (t-ZrO₂) phases. The peaks at $2\theta = 30$ is due to tetragonal structure, $2\theta = 29$ is monoclinic ZrO₂, $2\theta = 35$ is Monoclinic ZrO₂ and the rest of the peaks are due to monoclinic ZrO₂. For both the doped ceria and zirconia there is no evidence of separate Ru metal or RuO₂ phases (would appear between 25° and 42°). In our previous study⁴³ we have characterized using synchrotron-XRD (see SI Figure 5) to ensure ruthenium crystallographic phases (ruthenium metal or oxides) were not forming, which strongly suggests that the metal oxide is likely doped.

The measured BET surface area of 5% Ru doped CeO₂ (14.5 m²/g) was approximately 50% higher than 5% Ru doped ZrO₂ (9.5 m²/g) as shown in Table 1. SEM images (Figure 2) show micron-sized crystallites for 5% Ru doped CeO₂ and 5% Ru doped ZrO₂. Figure 3 (a) and (b) show the typical TEM image of 5%Ru doped CeO₂ and 5%Ru doped ZrO₂ samples. The 5%Ru doped CeO₂ (Figure 3 (a)) sample has regular shape and about 20 nm mean diameter. 5%Ru doped ZrO₂ has irregular shape and bigger aggregates, in the order of 100 nm (mean diameter). The characterization results indicated that Ru doped CeO₂ possesses small particle sizes (20 nm), high surface area (14.5 m² g⁻¹) compared with Ru doped ZrO₂ (100 nm and surface area, 9.5m² g⁻¹) prepared by same combustion method.

Table 2 shows the oxygen uptakes measured for the doped and undoped catalysts. The O₂ consumption obtained for 5% Ru doped CeO₂ catalyst was considerably higher than 5% Ru doped ZrO₂. Several studies reported that cerium oxide have a very high oxygen storage capacity³⁸⁻³⁹. This capacity is associated to the ability of cerium to act as an oxygen buffer by storing/releasing O₂ due to the Ce⁴⁺/Ce³⁺ redox couple³⁹. It has been reported that metal modified CeO₂ and ZrO₂ has a higher oxygen storage capacity and reducibility than pure CeO₂ and pure ZrO₂⁴⁰⁻⁴¹.

Chemical characterization of the catalyst

The chemical properties of the Ru doped CeO₂ and Ru doped ZrO₂ were studied by performing temperature-programmed reduction (TPR) with H₂ and CO, experiments.

a) Temperature-programmed reduction with H₂ (H₂-TPR)

Temperature programmed reductions were performed to characterize the reducibility of the samples. The Figure 4 shows the H₂-TPR reduction experiments of Ru doped CeO₂ and Ru doped ZrO₂ respectively. For the H₂-TPR of Ru doped CeO₂, the H₂ partial pressure starts decreasing as the temperature reached to 100 °C, and at the same time water signal observed in the mass spectrometer. The maximum amount of hydrogen consumed at 150 °C, and this correlates the maximum amount of water produced at the same temperature confirmed from the change in partial pressure of H₂ and H₂O and the overall H₂ uptake was 535 μmolg⁻¹. After 300 °C, the H₂ consumption decreases as the catalyst surface is already reduced and it makes more difficult to remove the oxygen from the surface. In case of Ru doped ZrO₂, the H₂ uptake starts at around 200 °C and the maximum H₂ reduction occur at much higher temperature 350 °C compare to Ru doped CeO₂ catalyst. The H₂ uptake calculation shows very low amount of H₂ was consumed (137 μmolg⁻¹), considering ZrO₂ is hardly reducible oxide (34 μmolg⁻¹). Which indicates that Ru doped CeO₂ is much more reduced than Ru doped ZrO₂ catalyst under similar conditions. In both the cases, the surface is reduced by H₂ and makes water. The presence of the Ru dopant makes the CeO₂ surface more reducible.

b) Temperature-programmed reduction with CO (CO-TPR)

Temperature-programmed reduction of Ru doped CeO₂ and Ru doped ZrO₂ was carried out with CO shown in Figure 5 and Figure 6. For Ru doped CeO₂ catalyst, CO oxidation starts at 70 °C and the maximum oxidation occur at 90 °C. First CO₂ formed with the reduced catalyst and H₂ is formed much later than CO₂ formation. However for Ru doped ZrO₂ catalyst, the CO oxidation starts at 200 °C and H₂ observed at 300 °C. This suggests that Ru doped CeO₂ much more reducible than Ru doped ZrO₂. For both the catalyst, water signal remains unchanged at all temperature when the H₂ signal appears. Therefore, we think that H₂ produced from the hydroxyls present on the catalyst surface and not from the reduction of water (by the reduced ceria surface⁴² or from the water–gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$)). We also noticed no H₂ is produced during pretreatment of the catalyst with Ar, even though water and hydroxyls are

present on the catalyst surface. Hence, we claim H_2 production is attributed to the fact that CO started reducing the surface; H_2 desorbs from the reduced surface.

Catalytic properties

Before evaluating the catalytic activity of Ru doped oxide catalyst, the undoped CeO_2 and undoped ZrO_2 were investigated as controls for partial oxidation of propane in the presence of CO_2 as the oxidant. Both the catalysts were inactive ($<2\%$ C_3H_8 conversion) for reaction with propane up to $T=550\text{ }^\circ\text{C}$. The activity of 5% Ru doped CeO_2 and 5% Ru doped ZrO_2 was investigated in the temperature range from 100 to $550\text{ }^\circ\text{C}$. The effect of temperature on propane conversion over different catalysts is shown in Figure 8. As the temperature increases, the conversion of propane increases. In the absence of CO_2 , very little propane conversion was observed for either catalyst, and propane was not converted at all below $450\text{ }^\circ\text{C}$. This suggests that propane is not directly oxidized by the catalyst in either case despite the fact that both catalysts oxidize hydrogen and CO. A low amount of propylene was also detected for both the catalysts at $550\text{ }^\circ\text{C}$, despite the fact that C-H bond dissociation can occur on ruthenium metal. Carbon balance calculated using the formula, moles of carbon in products/moles of carbon in reactant, was found to be $\sim 100\%$ under non-oxidative conditions for both the catalysts.

Under oxidative conditions, 5%Ru doped CeO_2 showed higher activity (53% conversion) compared to 5%Ru doped ZrO_2 (22% conversion, Figure 8). The major products detected were CO and H_2 (Figure 9). No propylene has been observed for both these catalysts. 5%Ru doped CeO_2 makes methane while 5%Ru doped ZrO_2 produce no methane. Propane dry reforming on noble metal-based Pt, Rh and Ru catalysts also studied by Solymosi et al.²⁷⁻²⁹. The dry reforming results suggest that Rh and Ru catalysts are the best among other noble catalyst for CO and H_2 production which correlates with our finding. In presence of CO_2 propane makes significant amount of H_2 and CO. Instead of dehydrogenation reaction, CO_2 reforming reaction takes place. Hence the results obtained from propane oxidation indicates a stronger surface sensitivity of the propane dry reforming reaction, suggesting that either C–C bond cleavage or C oxidation is the rate-determining step for propane reforming. With regard to the mechanism of the dry reforming of C_3H_8 over Ru/ Al_2O_3 , Ross et al.³⁴ assumed the fast and complete decomposition of C_3H_8 to carbon and its subsequent reaction with adsorbed O and OH formed in the dissociation of CO_2 . The results of the present study, however, showed that in the absence of CO_2 , the catalyst makes

CO, H₂ with small amount of propene only above 450 °C. However, addition of even a small amount of CO₂ to propane opened a new route of the reaction, namely the formation of H₂ + CO (Eq. (1)). This suggests that the adsorbed oxygen originating in the dissociation of CO₂ could be involved.

It must be noticed that CO₂ can be converted to CO via reverse water–gas shift reaction by consuming H₂ (Eq. (5)) or via Boudouard reaction by consuming coke on the catalyst surface (Eq. (6)).

The propane reactivity studies with CO₂ reveal that the activity of the doped oxide catalysts depends upon the type of host, propane to oxidant ratio and space time. CO₂ has biggest role in the partial oxidation of propane. As the oxidant (CO₂) to propane ratio increases, the catalytic activity increases and as well CO and H₂ formation increased. Low carbon balance was observed for both the catalyst which is due to coking of catalyst under reaction conditions.

The effect of the CO₂/C₃H₈ ratio on the performance of 5% Ru doped CeO₂ are shown in Figure 10. In these runs, the flow rate of propane is held constant and the flow rate of CO₂ and Ar are changed such that the sum of these is held constant. Hence the total inlet flow rate is kept constant and the space velocity is constant while the CO₂/C₃H₈ ratio is changed. The presence of CO₂ changes the reaction pathway of C₃H₈ and instead of dehydrogenation and cracking, the formation of H₂ and CO came into prominence. For a stoichiometric composition of reacting gas mixture, C₃H₈/CO₂ = 1:3, corresponding to the equation 1.

the H₂/CO ratio should be 0.66. In the experiments the reaction has been carried out with different stoichiometric ratio of CO₂ to propane (CO₂/C₃H₈= 1 to 4). The H₂/CO ratio changes depending the amount of CO₂ concentration. A much higher conversion, 87%, of C₃H₈ was achieved in the presence of a large excess of CO₂ (C₃H₈/CO₂ = 1:4). Higher amount of H₂/CO (0.76) observed at lower CO₂/C₃H₈ ratio (CO₂/C₃H₈= 0.5) and it decreases as the CO₂/C₃H₈ increases. With increased CO₂ content, the conversion of propane (82% at CO₂/C₃H₈=4) increased and the H₂/CO ratio decreases. Methane formation remains unchanged with increasing

CO₂ partial pressure. Low carbon balance (90%) observed due to coking of catalyst. High CO₂/C₃H₈ ratio favors CO production. For hydrogen and/or synthesis gas production, it is apparent that CH₄ is not a desirable product as the production of CH₄ competes with hydrogen generation.

CO₂ Methanation Reaction

In our previous publication³⁹, 5% ruthenium doped ceria was reported to be active for CO₂ methanation (equation 2) at relevant temperatures and pressures. It would follow that a significant amount of CH₄ would be formed when ample amount of CO₂ and H₂ are present; however during propane partial oxidation with CO₂, very small amounts of CH₄ are detected. This may be explained by two reasons: (1) a more oxidizing feed rich in CO₂ and (2) carbonate decomposition at higher temperatures. At temperatures below ~ 450 °C, the feed contains two moles of carbon dioxide (oxidant) for every one mole of propane (reductant). In the prior work, one mole of carbon dioxide was fed for every 4 moles of hydrogen (reductant), resulting in a catalyst that was more reduced at steady state. During propane partial oxidation, the more oxidized catalyst does not favor methane formation, which is consistent with the prior work showing the sensitivity of catalyst to the degree of reduction. This sensitivity is further demonstrated when pulses of carbon dioxide and hydrogen are passed over a reduced ruthenium doped ceria catalyst (Figure 10). The first pulse has the most carbon monoxide, which come from carbon dioxide reacting with the catalyst. As the degree of reduction changes as carbon dioxide is added, the activity changes to favor less carbon monoxide formation.

At temperatures above ~450 °C, the conversion increases, and more carbon monoxide (reductant) and hydrogen (reductant) are formed while carbon dioxide (oxidant) is consumed. However, at higher temperatures, the surface carbonates responsible for methane formation have been observed to be present in much lower concentrations on the catalyst.

It is also possible that CO could combine with hydrogen to form methane:

Methane has been observed when only CO and H₂ were exposed to oxidized 5% RuCeO₂; however this activity decreased with time (Figure 11). This is likely due to the reaction of CO

with lattice oxygen, creating CO₂, which can then react with hydrogen to form methane as described above. As the RuCeO₂ is reduced, the methane production becomes negligible. During propane partial oxidation, the RuCeO₂ is in the presence of reducing gases, propane, propylene, carbon monoxide, and hydrogen, so CO-methanation is expected to be negligible.

Effects of O₂ co-feed with CO₂ on propane reactivity

The data presented above for partial oxidation of propane was using carbon dioxide as a mild oxidant. Introduction of oxygen in the reaction mixture increases the catalyst activity and stability⁶⁻⁹. It has been observed that oxidative dehydrogenation of light alkanes in the presence of CO₂ is an endothermic process (e.g. for propane $\Delta H_{298\text{ K}} = +166.6\text{ kJ/mol}$), thus when small amount of oxygen is added to the system the energy demand decreases and also the coke formation is decreased by which the catalytic stability increases. Hence, a second test was then carried out by adding O₂ in small percentage in the feed, as in the proportions C₃H₈:CO₂:O₂: Ar = 1:2:0.25:4.75 and 1:2:0.25:4.5. When there is no O₂ in the feed, the conversion was 55% with CO₂ feed only. Noticeably, the initial propane conversion increased up to 70% (Figure 12) when O₂/C₃H₈ was 0.25. With further increase in O₂ concentration, propane conversion increased to 80%. The conversion of O₂ was almost 100% for all the duration of the run. The formation of CO (Yield =70%) and H₂ (Yield=27%) increased when both CO₂ + O₂ mixture were used as oxidant.

To probe the question of whether or not propane is dehydrogenated independently to produce propylene which in turn is reacted with the carbon dioxide, propylene reactivity was studied on the doped metal oxide catalysts. The activity was measured from 100 to 550 °C at temperature ramp rate of 20 °C/min under oxidative condition using CO₂ as oxidant. Under non oxidative condition, a low conversion of propylene (~17% at 550 °C) was observed for both 5% Ru doped ceria and 5% Ru doped zirconia catalysts and no significant differences were observed between the two catalysts (see Figure 1 in Supplementary Data). The major products observed were CO and H₂. Under oxidative conditions, propylene reacts in the presence of CO₂ to form CO and H₂. The ratio of H₂ to CO was ~ 0.27. At high temperature, 550 °C, the higher surface area 5% Ru doped CeO₂ showed a higher conversion (conversion ~ 45%) compared to 5% Ru doped ZrO₂ (conversion ~30%, see Figure 2 in Supplementary Data).

Catalyst Stability and Deactivation

Figure 13 shows the results from continuous operation of the catalysts tests carried out for 15 h over 5% Ru doped CeO₂ with a CO₂/C₃H₈ ratio equal to 2. The catalyst showed improved stability up to 1h (conversion = 52%) then the conversion decreased gradually with time on stream (after 15 h, conversion = 32%). However, the H₂/CO ratio remains unchanged (H₂/CO=0.73). When the reaction was carried out in presence of O₂ with CO₂, the catalyst showed higher activity (conversion = 62%) and better stability compared to the reaction with CO₂ only. The initial conversion was 62% then after 3 h the conversion decreased to 52% and remains steady up to 15 h on time on stream.

It has been observed that Ru based catalyst are active for propane partial oxidation to syngas. However the coke formation and active metal sintering are expected to cause deactivation of Ru based catalysts. The activity decreases with time on stream due to carbon deposition on catalyst surface. Hence it is high priority how to regenerate the catalyst from coking. Typically in industry, O₂ or air is used to oxidize coke in the regenerator⁴⁰. Literature suggests that the efficient coupling of air oxidation ($C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -394.5$ kJ/mol) and reverse Boudouard reaction ($C(s) + CO_2(g) \rightarrow 2CO(g)$, $\Delta H = 175.2$ kJ/mol), led to better regenerative operation for reducing catalyst sintering.

The carbon on the catalyst surface was oxidized by introducing oxygen to the catalyst bed. The carbon was converted to mostly CO₂ and partly CO detected by quadrupole mass spectrometer. The carbon on the catalyst was mostly oxidized at the temperature under 300 °C (Figure 14). The carbon formed in the catalyst might be carbon having small range order which burn at lower temperature. If the carbon is long range order (considered hard coke) then it should oxidized at higher temperature. But in our case the carbon deposited should be soft coke which decomposed at lower temperature.

4. Conclusions

Ceria and zirconia are relatively inactive for reactions with alkanes. Atomic doping with 5% Ru activates both metal oxides for partial oxidation of propane with carbon dioxide as an oxidant. The present work supports the following:

- 1) Both host oxides were inactive to propane and carbon dioxide when ruthenium was absent, doping with ruthenium increases C-C cleavage and dry reforming activity of propane at modest temperatures. Dehydrogenation to propylene was not observed.
- 2) Ruthenium doped ceria has higher oxygen mobility and was more reducible with hydrogen and carbon monoxide than ruthenium doped zirconia. However, both catalysts were unreactive towards propane below 300 °C and their activities were nearly identical above 300°C. We conclude that the reducibility of the oxide had no significant effect on the catalyst activity.
- 3) The surface morphologies of the two catalysts are very different and the particles sizes, and surface areas are different. RuCeO_x has been reported to contain many surface carbonates that participate in reactions, and RuZrO₂ does not contain carbonates. Despite these differences, the activity of the two catalysts are the same below 450 °C and comparable above that temperature. Despite incorporation into different host oxides, the ruthenium metal loading still has the largest effect on propane conversion. The low rate of dehydrogenation in the absence of carbon dioxide suggests that the chemistry is not identical to ruthenium on an inert support.
- 4) Co-feeding CO₂ substantially increased the activity for both catalysts and more CO was observed at high partial pressures of CO₂. Both catalysts suffered from deactivation from coke formation. The addition of 25% O₂ facilitated greater propane conversion, lower coke, and a greater syngas yield.

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Table 1: BET surface area for the doped catalysts after combustion at 550 °C.

Catalyst	Surface area (m ² /g)
5% Ru doped CeO ₂	14.5
5% Ru doped ZrO ₂	9.5

Table 2: O₂ uptake measured at 450 °C.

Catalysts	O ₂ uptake (μmol /g)	Molecules of O ₂ taken up / Total surface atoms
5% Ru doped CeO ₂	252	0.108
5% Ru doped ZrO ₂	174	0.075

Table 3: Amount of carbon deposited on the catalyst surface after propane partial oxidation at 550 °C.

Catalysts	Carbon formed (mg/g of catalyst)
5% Ru doped CeO ₂	11.9
5% Ru doped ZrO ₂	11.1

Table 4: H₂-TPR quantitative analysis results for the Ru doped catalysts⁴⁴.

Catalysts	H ₂ uptake (μmol /g)	ZrO ₂ /CeO ₂ (μmol /g) content in Catalyst	Content reducible CeO ₂ (μmol /g) ^a	Content reducible CeO ₂ (%) ^b
CeO ₂	342	5519.5		
ZrO ₂	34	7709.8		
5% Ru doped CeO ₂	535	5519.5	864	15.6
5% Ru doped ZrO ₂	137	7709.8	68	0.9

^a Calculated by $2 \times [\text{H}_2 \text{ Uptake} - 103]$, where the value 103 μmol.g⁻¹ is the H₂ uptake for the Ru metal; It should be noted that ZrO₂ is hardly reduced. H₂ uptake of Ru was calculated by subtracting the H₂ uptake by ZrO₂ from H₂ uptake by Ru doped ZrO₂ (137-34=103). ^b The reducible CeO₂/ZrO₂ percentage in the catalysts was calculated by $[\text{Reducible CeO}_2/\text{ZrO}_2 \text{ Content}]/[\text{CeO}_2 / \text{ZrO}_2 \text{ content of Catalyst}] \times 100\%$.

Figure 1(a): XRD diffractogram of CeO_2 and 5% Ru doped CeO_2 .

Figure 1(b): XRD diffractogram of ZrO_2 and 5% Ru doped ZrO_2 .

a) 5% Ru doped CeO₂

b) 5% Ru doped ZrO₂

Figure 2: Scanning electron micrographs of (a) 5% Ru doped CeO₂ and 5% Ru doped ZrO₂

Figure 3: TEM images of (a) 5%Ru doped CeO₂ and (b) 5%Ru doped ZrO₂

Figure 4: Temperature programmed reduction (TPR at 550 °C with a temperature ramp of 10 °C degrees per min) of 5% Ru doped CeO_2 and 5% Ru doped ZrO_2 exposed to H_2 (8ml/min) and Ar (7ml/min). Partial pressures are normalized by the partial pressure of Ar. The catalyst was pretreated in a flow of Ar at 500 °C for an hour.

Figure 5: Temperature programmed reduction (TPR) of 5% Ru doped CeO_2 , exposed to CO (8ml/min) and Ar (7ml/min). Partial pressures are normalized by the partial pressure of Ar. The catalyst was pretreated in a flow of Ar at 500 °C for an hour.

Figure 6: Temperature programmed reduction (TPR) of 5% Ru doped ZrO_2 , exposed to CO (8ml/min) and Ar (7ml/min). Partial pressures are normalized by the partial pressure of Ar. The catalyst was pretreated in a flow of Ar at 500 °C for an hour.

Figure 7: Conversion of propane normalized to surface area versus temperature during temperature programmed reaction (TPR) with a temperature ramp of 10 °C degrees per min from 100 °C up to 550 °C for preoxidized (air at 550 °C) catalysts with the space time 1 sec under oxidative conditions Propane:CO₂: Argon (1:2:5) on 5% Ru doped CeO₂ (●), 5% Ru doped ZrO₂ (○) and nonoxidative conditions, Propane: Argon (1:7) on 5% Ru doped CeO₂ (▲) and 5% Ru doped ZrO₂ (■). Note: The highest conversion for propane was 53% (550 °C) on 5% Ru doped CeO₂

Figure 8:(a) Surface area normalized yield of CO, H₂ and CH₄ on 5% Ru doped CeO₂ with the space time 1 sec under oxidative conditions (Propane: CO₂: Argon (1:2:5))

Figure 8: (b) Surface area normalized yield of CO, H₂ and CH₄ on 5% Ru doped ZrO₂ with the space time 1 sec under oxidative conditions (Propane: CO₂: Argon (1:2:5)).

Figure 9: Ratio of H_2/CO and CH_4/CO on 5% Ru doped CeO_2 varying CO_2 partial pressure at constant propane partial pressure with space time 1 sec, $\text{CO}_2 : \text{C}_3\text{H}_8 = 0.5$ to 4, Temperature = 550°C .

Figure 10: 1 mL pulses of 4:1 H_2/CO_2 in 10 ccm argon carrier gas at 350°C on 5% Ru doped CeO_2 (H_2 not shown). Pre-treatment: 5 hours in 10% CO at 350°C , followed by brief heating in Argon to 550°C to decompose any carbonates that formed. In the first pulse where the catalyst is most reduced, the most CO_2 is consumed to make CO . In the following pulses, as the catalyst is being oxidized, less CO is made and more methane is made.

Figure 11: CH₄ and CO₂ from constant H₂ and CO addition on Ru doped CeO₂ at 350°C on 5% Ru doped CeO₂. Initially, CO is converted CH₄ (likely by first being oxidized by the catalyst oxygen to CO₂, then to methane) until the lattice oxygen is depleted. The catalyst had been oxidized with 4:1 H₂/CO₂ at 350 °C and purged before introduction of feed gases at time 0:00.

Figure 12: Yield of CO, H₂ and CH₄ on 5% Ru doped CeO₂ varying O₂ partial pressure at constant propane and CO₂ partial pressure with space time 1 sec, O₂:CO₂ : C₃H₈ = 0.125:2:1 and O₂:CO₂ : C₃H₈ = 0.25:2:1. Temperature = 550 °C.

Figure 13: Stability test of 5% Ru doped CeO₂ in presence and absence of O₂ with space time 1 sec, CO₂: C₃H₈ = 2:1 and O₂:CO₂: C₃H₈ = 0.25:2:1, Temperature = 550 °C.

Figure 14: (a) CO and CO₂ peak from coke testing after propane oxidation on 5%Ru doped ZrO₂.

Figure 14: (b) CO and CO₂ peak from coke testing after propane oxidation on 5%Ru doped CeO₂.