



# Different reaction sequences for partial oxidation of propane over different ceria-supported catalysts



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## ABSTRACT

Hydrogen production using the partial oxidation of propane over supported metal catalysts was studied in a small isothermal packed-bed reactor. Ceria was used as the support, due to its ability to store and release oxygen, with nickel and platinum being the metals used. The overall purpose of the study was to determine the pathways and sequences of hydrogen production. Flow rates of the inlet stream were varied from 100 to 400 scc/min, and two weights of each catalyst were used. The reactions were carried out at 600 °C and 1 atm, with a ratio of O<sub>2</sub> to C<sub>3</sub>H<sub>8</sub> maintained at 1.78. For the experimentally observed products leaving the reactor, the corresponding reaction matrix was subjected to Gauss elimination to determine that four independent reactions could be obtained. This results in a maximum of ten sets of these reactions. The number of sets was reduced by carrying out a material balance on the products to determine the net rate of each of the four reactions; sets containing negative rates for irreversible reactions could then be eliminated from consideration. To determine the validity of any remaining sets containing dry-reforming, steam-reforming and water-gas shift reactions, a secondary set of experiments were carried out at the outlet conditions of the original experiments to see if those three reactions could indeed take place. Eventually, only one set of four reactions was deemed suitable for the Pt/CeO<sub>2</sub> catalyst, incorporating total oxidation, partial oxidation, dehydrogenation and water formation. The extents of these four reactions were followed as a function of contact time, showing that partial oxidation decreases down the reactor, while total oxidation increases. For the Ni/CeO<sub>2</sub> catalyst, three sets were suitable. The three are very similar, in that they all contain total oxidation, steam reforming and dehydrogenation, with the fourth reaction being partial oxidation, dry reforming or water formation. Qualitatively, the same results are found for all three sets. Total oxidation is the predominant reaction at all contact times, with steam reforming and/or dry reforming producing hydrogen only at larger contact times. The differences between the results for the two supported catalysts indicate that different types of reactors should be chosen, depending upon the catalyst to be used. For supported nickel catalysts, large packed-bed reactors may be optimal, while micro-reactors in parallel may be best for supported platinum catalysts.

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**Abbreviations:** AT, Rautothermal reforming; CD, carbon deposition; CF, coke formation; CR, cracking; DH, dehydrogenation; DR, dry reforming; GC, gas chromatograph; HAS, high surface area; LSA, low surface area; ME, methanation; POX, partial oxidation; SR, steam reforming; TOX, total oxidation; WF, water formation; WGS, water-gas shift; WHSV, weight-hourly space velocity.

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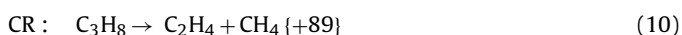
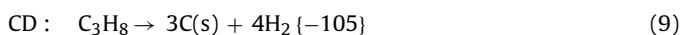
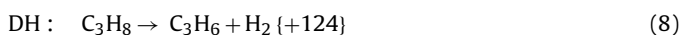
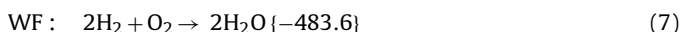
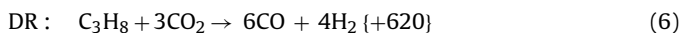
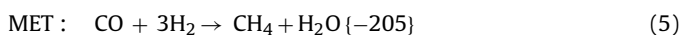
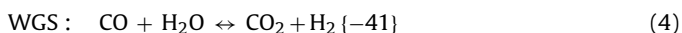
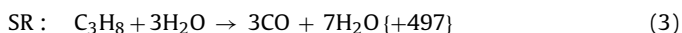
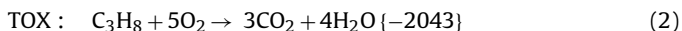
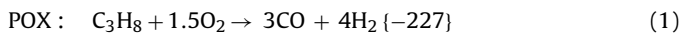
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## 1. Introduction

Hydrogen production from hydrocarbons is an area of research that has waxed and waned in importance through several cycles in recent years. There are advantages to hydrogen as a fuel source, notably its lack of polluting byproducts and impurities. Disadvantages include difficulties in storage and transportation to its point of use. Hence there is a case that can be made for using easily transportable hydrocarbons, such as gasoline, as a source to product hydrogen at its point of use.

However, catalytic oxidation of hydrocarbons yields not only hydrogen, but a number of products through a complex set of competing reactions. These include the primary reactions partial oxidation (POX) and total oxidation (TOX); as well as secondary reactions involving products of the primary reactions: steam

reforming (SR), water-gas shift (WGS), methanation (MET), dry reforming (DR), water formation (WF), and finally unimolecular reactions involving only the hydrocarbon: dehydrogenation (DH), carbon deposition (CD), and cracking (CR). In this work, we use propane as a model for gasoline; the reactions can then be written as:



where the numbers in brackets {} denote the standard enthalpy change of the reaction, in [kJ/mol].

Given the number of possible reactions, it is of value to analyze the processes occurring in the reactor, specifically, the order in which they occur. Clearly, there are two main possibilities [1]. In the first, TOX occurs first, to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ; this is then followed by secondary reactions such as SR and DR, to form the  $\text{H}_2$ . A second possibility is that POX occurs first, or at least in parallel with TOX. The literature contains multiple examples of experiments purporting to show the existence of only one pathway or another. These papers have been summarized recently [2] and are not repeated here. The question is now how to analyze the kinetic data that can be obtained in a laboratory reactor in order to answer this question.

A corollary is to ask how kinetic data can be analyzed with that many reactions. This is a general question that can be applied to several other complex reaction networks. In this work, we develop further a technique we used earlier in a preliminary fashion [2] to analyze output from propane oxidation over Pt supported on ceria supports of different surface areas. We repeat these runs and re-analyze these data, and also analyze data using Ni/ceria. Both Pt and Ni are useful metals for DH reactions. Ceria was used as a support as it is extensively used in automobile three-way catalysts for partial oxidation, and the cerium shows an easy transition between the  $\text{Ce}^{+4}$  and  $\text{Ce}^{+3}$  states. In brief, the approach used here is to analyze the products formed at different loadings of Pt/ $\text{CeO}_2$  and Ni/ $\text{CeO}_2$  at different flow rates at a fixed temperature and a fixed  $\text{O}_2/\text{C}_3\text{H}_8$  ratio to obtain the effect of contact time. The results indicate which sets of independent reactions are feasible, and if secondary reactions can occur under reactor-outlet conditions. Accordingly, the sequence of TOX and POX (or equivalent) reactions is determined.

## 2. Materials and methods

### 2.1. Materials

The catalysts used were 1% Pt/ $\text{CeO}_2$  and 1% Ni/ $\text{CeO}_2$ . The support was prepared in-house by precipitation from cerium nitrate and ammonium hydroxide solutions. In the previous work [2], we had also used ceria obtained from Aldrich, with a lower surface area as a support for the Pt. To make the distinction clear, we label the previous catalysts as 1% Pt/ $\text{CeO}_2$  (low surface area, LSA) and 1% Pt/ $\text{CeO}_2$  (high surface area, HSA), while the current catalysts are 1% Pt/ $\text{CeO}_2$  (HSA), and 1% Ni/ $\text{CeO}_2$  (HSA). In all cases, the

metals were added by incipient wetness, using tetramine platinum (II) nitrate ( $\text{Pt}(\text{NH}_4)_4(\text{NO}_3)_2$ ) and nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ). Further details are found in Refs. [2–4]. Characterization details are also found in Refs. [2–4].

### 2.2. Reactor and method for primary reactions

A simple microreactor setup with a gas chromatograph (GC) was used to carry out the reactions. The main reactions studied were those where propane and oxygen were the reactants. Three tanks were used, one containing pure Ar, one containing 30%  $\text{O}_2$  and 70% Ar, and one containing 10%  $\text{C}_3\text{H}_8$ , 10%  $\text{N}_2$  and 80% Ar. Of the inlet gases, the experimental design called for 90% inerts (argon and nitrogen); of the reactants, the ratio of  $\text{O}_2$  to  $\text{C}_3\text{H}_8$  was maintained at 1.78. This was low enough to be out of the explosive range (2–10) and yet containing a significant amount of propane. For a total flow rate of 300 scc/min, these conditions were met by a flow of 128 scc/min from the Ar tank, 64 scc/min from the  $\text{O}_2$ -Ar tank and 108 scc/min from the  $\text{C}_3\text{H}_8$ - $\text{N}_2$ -Ar tank, using separate mass-flow controllers. The reactor was a quartz tube placed in a single-zone furnace. The supported catalyst was mixed with fine quartz and the combination was sandwiched between quartz wool in the reactor tube. The experiments discussed in this work were carried out at 1 atm. Outlet gases ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$  and  $\text{O}_2$ ) were passed through a cold trap and then to the GC where the reactants and products (except  $\text{H}_2\text{O}$ ) were analyzed by a thermal-conductivity detector and a flame-ionization detector. Further details can be found in Ref. [4].

The catalysts were reduced inside the reactor prior to use. This was carried out in a flow of 75 scc/min of pure  $\text{H}_2$  for 3 h. Prereduction was at 500 °C for the Ni catalysts and at 400 °C for the Pt catalysts. Then Ar was allowed to flow through the reactor, also at 75 scc/min for 3 h.

Preliminary runs carried out with the support alone showed that the main product is  $\text{CO}_2$ , and that is present in very small amounts. In another series of runs, the temperature was changed from 300 °C to 800 °C, this time over the supported metal catalysts. For both Pt and Ni, two zones exist. Below 500 °C,  $\text{CO}_2$  is the main product. Above 500 °C,  $\text{CO}$  and  $\text{H}_2$  are formed in increasing amounts. Oxygen is completely consumed at 500 °C. The final set of preliminary runs was carried out as a function of time at 800 °C, the highest temperature used. The catalysts were seen to be stable for at least 20 h.

Following these experiments, the primary reactions were run at 600 °C. Here, both mechanisms would be seen to exist, and the catalyst could be considered to be stable.

In order to determine the effect of contact time, two loadings (amounts) of the 1% supported-metal catalysts were placed into the reactor. For the Ni/ $\text{CeO}_2$  (HSA), 0.05 g and 0.10 g were used. For the Pt/ $\text{CeO}_2$  (HSA) and Pt/ $\text{CeO}_2$  (LSA), being the more-active catalysts, only 0.01 g and 0.02 g were needed. For each of these two loadings, the total flow rate of the inlet gases was increased from 100 to 400 scc/min, in increments of 100 scc/min. Based on the flowrates of each of the products and reactants ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$  and  $\text{O}_2$ ) leaving the system, the rates of appropriate sets of reactions (1)–(10) could be obtained in terms of the flow rate and loading, i.e., the contact time, or weight-hourly space velocity (WHSV). The notion of “appropriate sets” is dealt with in Section 3, immediately below.

Interestingly, in all of the experiments performed, neither  $\text{C}_2\text{H}_4$  nor  $\text{CH}_4$  were observed. Accordingly, in what follows, we consider that neither CR nor MET is observed under the conditions of the experiments performed here. No significant amounts of carbon were seen to be deposited; hence CD is also considered not to be observed.

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