DIFFERENT REACTION SEQUENCES FOR PARTIAL OXIDATION OF PROPANE OVER DIFFERENT CERIA-SUPPORTED CATALYSTS

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Submitted to Catalysis Today: May 31, 2015

Revised: October 7, 2015

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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 100-400 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 O₂ to C₃H₈ 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/CeO₂ 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/CeO₂ 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.

Keywords: partial oxidation; supported metal catalyst; reaction sequence; propane; hydrogen

1. Introduction¹

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:

¹ Abbreviations: ATR, autothermal 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.

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 CO_2 and H_2O ; this is then followed by secondary reactions such as SR and DR, to form the 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 Ce^{+4} and Ce^{+3} states. In brief, the approach used here is to analyze the products formed at different loadings of Pt/CeO₂ and Ni/CeO₂ at different flow rates at a fixed temperature and a fixed O₂/C₃H₈ 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. Material and Methods

2.1 Materials

The catalysts used were 1% Pt/CeO₂ and 1% Ni/CeO₂. 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/CeO₂ (low surface area, LSA) and 1% Pt/CeO₂ (high surface area, HSA), while the current catalysts are 1% Pt/CeO₂ (HSA), and 1% Ni/CeO₂ (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% O₂ and 70% Ar, and one containing 10% C₃H₈, 10% N₂ and 80% Ar. Of the inlet gases, the experimental design called for 90% inerts (argon and nitrogen); of the reactants, the ratio of O₂ to C₃H₈ 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 O₂-Ar tank and 108 scc/min from the C₃H₈-N₂-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 (CO, H₂, CO₂, H₂O, C₃H₈, C₃H₆ and O₂) were passed through a cold trap and then to the GC where the reactants and products (except H₂O) 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 H₂ for 3 hours. 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 hours.

Preliminary runs carried out with the support alone showed that the main product is 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 , CO_2 is the main product. Above 500°C , CO and H_2 are formed in increasing amounts. Oxygen is completely consumed at 500°C . The final set of preliminary runs were 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/ CeO_2 (HSA), 0.05 g and 0.10 g were used. For the Pt/ CeO_2 (HSA) and Pt/ 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 (CO , H_2 , CO_2 , H_2O , C_3H_8 , C_3H_6 and O_2) leaving the system, the rates of appropriate sets of reactions (1) through (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 C_2H_4 nor 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.

2.3 Method for Secondary Reactions

Reactions using C_3H_8 and O_2 were carried out initially. However, it was later necessary to use other reactants, to see if secondary reactions (such as SR, DR and WGS) could occur in appreciable amounts under the conditions of the reactor outlet. These reactions were carried out using the same experimental set up as described here. However, compositions of the inlet were changed to suit the particular reaction being checked as occurring (or not). These details are described later in Section 4.

3. Theory and Calculations

3.1 Number of independent reactions

This treatment was provided in an earlier work [2]. However, for completeness, it is included here.

While many reactions can be seen as being theoretically possible for any given set of reactants and products, it is axiomatic that there is a smaller set of independent reactions under these conditions, such that a member of this smaller set cannot be obtained by algebraic manipulation

of the remaining members. As a trivial example, for C, O₂, CO and CO₂, the following are possible reactions:

Of these, reaction (11d) is clearly not independent, being obtained by multiplying reaction (11b) throughout by 2. Of the remaining three, only two are independent; for example, reaction (11a) can be obtained by adding reactions (11b) and (11c). However, it is worth noting that (11b) and (11c) are only one set of two independent reactions; (11a) and (11b) could equally well be considered to be the set, as could (11a) and the reverse of (11c).

Similarly, for reactions (1) - (4) and (6) - (8) (with (5) (9) and (10) removed as explained above in Section 2), there is a smaller set of reactions which are independent. However, the actual reactions that occur could be expected to change, depending upon experimental conditions; hence additional experiments may be needed to determine which combinations of reactions are possible (or, at least, not impossible). Then these reactions may be used to determine how the overall complex reaction set proceeds. This is the motivation of the present work.

The mathematical construct for determining the number of independent reactions for a given set of reactant and products is the matrix technique of Gauss elimination [5]. We start with a matrix M_I of stoichiometric coefficients of reactions (1) - (4) and (6) - (8):

Reaction/Component	C ₃ H ₈	O ₂	CO ₂	CO	H ₂	H ₂ O	C ₃ H ₆
POX	-2	-3	0	6	8	0	0
TOX	-1	-5	3	0	0	4	0
SR	-1	0	0	3	7	-3	0
$M_I =$ DR	-1	0	-3	6	4	0	0
WGS	0	0	1	-1	1	-1	0
WF	0	-1	0	0	-2	2	0
DH	-1	0	0	0	1	0	1

(12a)

Subsequent matrix reduction steps reduce the number of non-zero rows and hence the rank of the matrix, until matrix M_2 of rank = 4 is obtained:

	1	0	0	0	-1	0	-1
	0	1	0	0	2	-2	0
	0	0	1	0	3	-2	- 0.33
$M_2 =$	0	0	0	1	2	-1	- 0.33
	0	0	0	0	0	0	0
	0	0	0	0	0	0	0

(12b)

$$0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0$$

Hence four independent reactions exist.

As mentioned above, any four reactions from the seven reactions (1) - (4) and (6) - (8) can be used. This amounts to 35 possibilities. However, the number can be brought down to a more manageable level by experimental observations. First, C_3H_6 is always observed in the experiments; hence one of the four reactions must be DH, reaction (8). Further, it is reasonable to assume that complete oxidation is always occurring; hence another required reaction must be TOX, reaction (2). This brings down the number of possibilities to 10, since each set must contain DH and TOX. The 10 possibilities are given in Table I, labeled as Sets I to X.

3.2 Reaction Rates from Formation Rates of Components

The rates of formation of each component in each reaction are related by stoichiometry. Thus for Set I, the rate of the POX reaction, R_{POX} , is related to the rates of formation of C_3H_8 (r_{POX,C_3H_8}), O_2 (r_{POX,O_2}), CO ($r_{POX,CO}$), and H_2 (r_{POX,H_2}) due to that reaction by:

$$R_{POX} = (1) r_{POX,C_3H_8} = (2/3) r_{POX,O_2} = (1/3) r_{POX,CO} = (1/4) r_{POX,H_2} \quad (13)$$

Similar relations can be written for the rates of TOX, WGS and DH, R_{TOX} , R_{WGS} and R_{DH} respectively, for Set I. Then the total rate of formation of any component leaving the reactor can

be obtained by summing the corresponding rates of formation over all four reactions in that set.

Thus for Set I:

$$\begin{aligned} r_{\text{C}_3\text{H}_8} &= r_{\text{POX},\text{C}_3\text{H}_8} + r_{\text{TOX},\text{C}_3\text{H}_8} + r_{\text{WGS},\text{C}_3\text{H}_8} + r_{\text{DH},\text{C}_3\text{H}_8} \\ &= R_{\text{POX}} + R_{\text{TOX}} + 0 + R_{\text{DH}} \end{aligned} \quad (14a)$$

noting that the zero term arises in the righthand side of Eqn (14a) because C_3H_8 is not a component in the WGS reaction. Similarly for the other components leaving the reactor:

$$r_{\text{O}_2} = 1.5 R_{\text{POX}} + 5 R_{\text{TOX}} \quad (14b)$$

$$r_{\text{H}_2} = 4 R_{\text{POX}} + R_{\text{WGS}} + R_{\text{DH}} \quad (14c)$$

$$r_{\text{CO}_2} = 3 R_{\text{TOX}} + R_{\text{WGS}} \quad (14d)$$

$$r_{\text{CO}} = 3 R_{\text{POX}} - R_{\text{WGS}} \quad (14e)$$

$$r_{\text{C}_3\text{H}_6} = R_{\text{DH}} \quad (14f)$$

Eqns (14) are six relationships between the experimentally determined rates of formation (on the lefthand side) and the (unknown) rates of the four reactions participating in Set I. The problem is over-constrained, hence the best values for the rates can be determined by a least-squares solution. Note that the equations do not include a relationship for the rate of formation of H_2O .

This is because this component was not measured experimentally. It can be calculated by difference, but there is no need, since the problem is already over-constrained.

Equations (14) and the analogs for the remaining sets, Sets II through X, are shown in Table II. Experimental data, using the materials and methods of Section 2 above, can be used as shown in Section 4 below to obtain the rates of the four independent reactions for each set (R_{POX} , R_{TOX} , R_{WGS} and R_{DH} for Set I).

If more than one set yields acceptable values for the four independent reactions, then further information would be needed if it were necessary to distinguish between the sets.

3.3 Negative Reaction Rates

It is expected that the value of these rates would be, for the most part, positive. A negative value of any one of these rates would seem to indicate that the set in question, while still acceptable as a set of independent reactions, would not be a suitable tool for understanding what is going on during the reaction. An exception to this rule would be the water-gas shift reaction, Eqn (4), which is known to be reversible.

Whether or not a negative reaction rate is reasonable can be quantified by comparing the values of the outlet activity ratio, $J_{\text{a,out}}$, defined as:

$$J_{\text{a,out}} \equiv \prod (a_{\text{i, out}})^{v_i} \quad (15a)$$

and the thermodynamic equilibrium constant, K_a , defined as :

$$K_a \equiv \exp [-\Delta G^\circ / (RT)] \quad (15b)$$

Here the product in Eqns (15a) and (15b) is over all components, a_i is the activity of component i at reactor outlet conditions (and can be taken to be the mole fraction of i for an ideal gas), ν_i is the stoichiometric coefficient of i in the reaction of interest, and ΔG° is the standard Gibbs free energy of formation for the reaction of interest. If :

$$J_{a,out} > K_a \quad (15c)$$

then the reaction is proceeding in the reverse reaction than as written, and a negative value of the reaction rate (say R_{WGS}) is feasible.

4. Results and Discussion

4.1 Outlet Flow Rates

Outlet volumetric flow rates were obtained for all components leaving the reactor, following the experiments described above in Section 2. The effects of time and temperature have been described earlier over the supported Pt catalysts [3] and over the supported Ni catalysts [4] and will not be repeated in this work. The results described and discussed here are the effects of

reactant flow rate and catalyst weight (loading). These parameters influence the weight-hourly space velocity (WHSV, feed rate per unit mass of catalyst) and its inverse, the contact time of the reactants with the catalyst. These runs were also carried out in a preliminary fashion earlier [2].

Figure 1 shows the effect of inlet flow rate on the flow rates of all outlet components except H_2O for 0.05g of the 1% Ni/CeO₂ (HSA) catalyst. Data for the loading of 0.1g of this catalyst, and for loadings of 0.01g and 0.2 g of the 1% Pt/CeO₂ (HSA) catalyst are available elsewhere [4]. In Figure 1, it is noteworthy that the production of the desired products H_2 and CO decreases with increasing reactant flow rates. This indicates that hydrogen production is favored at lower flow rates and at smaller contact times.

4.2 Reaction Rates

The difference between outlet and inlet flow rates for a component i is used as a measure of the formation rate, r_i , for that component. (Note that it is not a specific reaction rate, i.e., the amount of catalyst is not considered; this is carried out later.) Then the rates of the individual reactions, R_{POX} , R_{TOX} , etc., can be obtained from the relations in Table II.

MATLAB was used to obtain the best fit for the individual reactions. However, R_{DH} was set identically equal to $r_{\text{C}_3\text{H}_6}$, to ensure that the fitting procedure did not result in a negative value for that parameter. Tables III and IV summarize the results for the two loadings of the Ni/CeO₂ (HSA) catalyst for the different inlet flow rates, V_{inlet} . Tables V and VI show the corresponding values for the Pt/CeO₂ (HSA) catalysts. Similar results were reported earlier for Pt/CeO₂ (HSA) and Pt/CeO₂ (LSA) [2], but the preliminary analysis was carried out for an abbreviated number of sets, 6, as opposed to all 10 being considered in Tables V and VI.

4.3 Possible Reaction Sets

In Tables III and IV, Sets III, VI, IX and X have negative values for either DR or WF. It is not reasonable for these reactions to proceed in the net negative direction, so these sets may be discarded. Further, Set V has negative values for WGS but, as mentioned above, this is not unfeasible. However, applying the test of Eqn (15) under the conditions of Tables III and IV,

$$J_{a,out} = 0.4 < 2.5 = K_a \quad (16)$$

(Calculation details can be found in Ref [4].) Hence WGS, if it occurs, would not be expected to be proceeding in the negative direction. Accordingly, Set V may also be discarded. Positive values for all values of R are observed for Sets I, II, IV, VII and VIII. Hence these are possible choices for the set of four independent reactions for the Ni-based catalysts. Similarly, for the Pt-based catalysts, Sets VI, VII and IX are possible choices for the set of four independent reactions.

4.4 Use of Secondary Reactions to discriminate between Reaction Sets

To discriminate further between the five possible sets for the Ni-based catalysts and the three possible sets for the Pt-based catalysts, we need to examine the possibility (or otherwise) of the various secondary reactions, i.e., other than TOX and POX. Inspection of Sets I, II, IV, VII and VIII indicates that runs need to be made to test if any of SR, DR and WGS could be occurring in significant amounts over the Ni-based catalysts. Similarly, after inspection of Sets VI, VII and IX, DR and SR runs were carried out over the Pt-based catalysts. In all cases, the inlet conditions for these runs were chosen to simulate the outlet conditions of the reactor corresponding to the results of the oxidation reactions as shown in Tables III-VI. (Since H₂O was not explicitly measured, its flow rate leaving the oxidation reactor was estimated by difference.)

For the secondary reactions, the total inlet volumetric flow rate was kept at 300 scc/min and the reaction temperature was varied through 150°C around 600°C. Inlet flow rates for the components of these reactions were determined by the outlet values of the appropriate components (e.g., CO₂ and C₃H₈ for DR) leaving the oxidation runs with 300 scc/min inlet flow rate over the corresponding catalyst. The inlet flow rates for the runs testing secondary reactions are given in Table VII.

4.4.1 Supported Ni Catalysts

Figures 2 and 3 show the DR activity over the two loadings of the 1% Ni/CeO₂ (HSA) catalyst as a function of temperature. There are increases in DR products CO and H₂ with an increase in temperature and catalyst loading, and decreases in reactants CO₂ and C₃H₈. Quantitatively, at 600°C, conversions of CO₂ are 37% for the 0.05 g loading and 44% for the 0.1 g loading. Of the CO₂ converted, the corresponding yields of CO are 82% and 91% for the two loadings. More details can be found in [4]. Clearly, DR cannot be neglected as one of the reactions on the 1% Ni/CeO₂ (HSA) catalyst.

The results of SR reactions can be seen in Figures 4 and 5 for the two loadings of the 1% Ni/CeO₂ (HSA) catalyst. In both cases, while the conversion of C₃H₈ increases with temperature, the amounts of CO and H₂ formed are seen to decrease. Concurrently, increasing amounts of CH₄, C₂H₄ and C₃H₆ are observed. Quantitatively, the conversion of C₃H₈ is low for both loadings. However, at least at the higher temperatures, the amounts of CO and H₂, though low, are not negligible. More details can be found in [4]. Hence SR cannot be ruled out as one of the reactions on the 1% Ni/CeO₂ (HSA) catalyst.

WGS reactions were carried out in a similar fashion over the 1% Ni/CeO₂ (HSA) catalysts.

While the flow rate of reactant CO was decreased with increasing temperature, no CO₂ could be detected. Small amounts of H₂ were detected. At least for the 0.05 g loading, the catalyst was observed to have turned completely black. It would appear that WGS selectivity is very poor, and the H₂ is formed as a consequence of coking. Hence, WGS is not a part of the appropriate sets of reactions over the catalyst.

Accordingly, for the 1% Ni/CeO₂ (HSA) catalysts, Sets I and VIII can be discarded. Sets II, IV and VII are possible appropriate sets for C₃H₈ oxidation and can be examined further for the effect of contact time.

4.4.2 Supported Pt Catalysts

In Figures 6 and 7 are shown the results for DR reactions over the two loadings of the 1% Pt/CeO₂ (HSA) catalysts. Both CO and H₂ are detected, and the amounts generally increase with temperature and loading. However, total CO₂ conversions at 600°C are low – 16% for the 0.01 g loading, and 19% for 0.02 g loading. Yields of CO are also low, 26% and 34% for the two loadings, with a significant amount of coke formation observed. Hence DR is probably not appropriate as one of the reactions in a suitable set. Accordingly, Set IX can be discarded for the supported Pt catalysts.

Finally, we consider SR reactions for the Pt catalysts. In these runs, CO was observed only for the higher loading and only when the temperature was maintained at 600°C or above. For the lower loading, C₂H₄ was observed at all temperatures, but only in small amounts, and C₃H₆ was observed only at the highest temperatures. At the higher loading, CH₄ and C₂H₄ were observed only at the highest temperatures, while C₃H₆ was observed at all temperatures. More importantly,

in all cases, the catalyst was blackened, at least to some extent. Clearly SR is not an appropriate reaction. Hence Set VII can also be discarded for the supported Pt catalysts.

With Sets VII and IX deemed unsuitable, Set VI is the only possible set of reactions to be considered for oxidation reactions involving C_3H_8 over the 1% Pt/CeO₂ (HSA) catalysts. This is consistent with the preliminary results of Ref. [2].

4.5 Effect of Contact Time

Finally we consider the significance of the numerical values of R_{POX} , R_{TOX} , and the other values in the allowable sets of Tables III-VI. As mentioned earlier in [2], these represent the rates (in [scc/min]) of the corresponding reactions. Changes in these values with the different inlet flow rates V_{inlet} [scc/min] are due to two factors: the increasing amount of propane entering the reactor in a given amount of time, and the decreasing amount of time the reactants contact the catalyst. The former effect can be accounted for by multiplying the values of R_{POX} , etc., by a factor f , where:

$$f = 100 / V_{inlet} \text{ [scc/min]} \quad (17a)$$

such that:

$$R' = R f \quad (17b)$$

and R' represents the rate of reaction per 100 scc/min of inlet. The effect of the loading of catalyst can be accounted for by defining the weight-hourly space velocity (WHSV) as:

$$WHSV = V_{inlet} / m \quad (18)$$

where m represents the catalyst loading.

4.5.1 Supported Ni Catalysts

As shown in Section 4.4.1 above, Set II, IV and VII are appropriate sets for C_3H_8 oxidation over 1% Ni/CeO₂ (HSA) catalysts. The values of R_{POX} , R_{TOX} , R_{SR} , R_{DR} and R_{DH} are given as functions of V_{inlet} in Tables III and IV. The corresponding values of R' as functions of WHSV are given in Figures 8, 9 and 10 for Sets II, IV and VII respectively.

For all the sets, TOX is higher than the other reactions, with SR next. But as WHSV increases (or as contact time decreases), SR decreases much more than TOX. The rate of dehydrogenation, represented by R'_{DH} , is small, and remains essentially unchanged over the range of WHSV values. Values of the rate of the fourth reaction (POX, DR and WF for Sets II, IV and VII respectively) lie between R'_{DH} and R'_{SR} and are also relatively constant.

These results are in accordance with the results seen in Figure 1, where the 1%Ni/CeO₂ (HSA) catalyst shows higher selectivity towards CO and H₂ at the lowest flow rate of 100sccm (also the highest contact time). The results of Figures 8 through 10 show that the 1%Ni/CeO₂ (HSA) catalyst is most effective for hydrogen production at the highest contact times (lowest WHSV). At the highest WHSV, or the lowest contact times, the main reaction is TOX. But as contact time increases, there is only a small increase in R'_{TOX} but a large increase in R'_{SR} . SR is an endothermic reaction (see Eq 3), deriving the energy it requires from the energy generated by the exothermic TOX reaction (see Eq 2). Moreover, the feed for the SR reaction is produced from the TOX reaction. Hence, SR comes into action only at higher contact time, as this reaction needs reactants and energy. This is supported by an increase in R'_{SR} at higher contact times.

Up to this point, we have not distinguished between the three sets, Sets II, IV and VII. All the sets contain TOX, SR and DH. In addition, for the fourth reaction, Set II contains POX, Set IV

contains DR, and Set VII contains WGS. Whether the fourth reaction is POX or DR or WF, qualitatively the results are the same. This is because, at lower WHSV values, the predominant reactions are only TOX and SR. At higher values of WHSV, the values of R'_{POX} or R'_{DR} or R'_{WF} are still very low compared to R'_{TOX} . POX consumes O_2 and C_3H_8 , while DR consumes C_3H_8 , and WF consumes O_2 . Hence, any of these reactions can only affect the extent of TOX, which has C_3H_8 and O_2 as reactants, and which remains essentially the same for all the three cases. Also, the extent of SR shows a similar trend and values over the entire span of WHSV for all 3 sets. Hence, irrespective of the fourth reaction, the sets yield the same results. The main reaction favoring hydrogen production over the Ni-based catalyst is the (endothermic) SR, supported at the higher contact times. Accordingly, the 1%Ni/CeO₂ (HAS) catalyst can be seen to be effective for H₂ production at the highest contact times, and proceeds through the indirect POX route.

4.5.2 Supported Pt Catalysts

Following Section 4.4.2, only Set VI can be considered appropriate for C_3H_8 oxidation over 1% Pt/CeO₂ (HSA) catalysts. The values of R_{POX} , R_{TOX} , R_{SR} , R_{DR} and R_{DH} are given as functions of V_{inlet} in Table V and VI. The corresponding values of R' as functions of WHSV are given in Figure 11.

Figure 11 indicates that R'_{TOX} decreases with an increase in WHSV, whereas there is a slight increase in R'_{POX} . R'_{WF} increases with an increase in WHSV, while values for R'_{DH} are small and relatively unchanged over the range of WHSV values.

This denotes that, for the 1%Pt/CeO₂ (HSA) catalyst, an increase in the contact time between the reactants and catalyst (i.e. a decrease in WHSV) increases TOX rates within the reactor. POX is comparatively higher at lower contact times. This is consistent with the results in Ref [2]. Figure

11 demonstrates that the 1%Pt/CeO₂ (HSA) catalyst is most effective for hydrogen production at the higher flow rates, or lower contact times. On the other hand, the catalyst is most effective for TOX at lower flow rates or higher contact times. Accordingly, the POX reaction occurs before (or in parallel with) the TOX reaction. Therefore, for 1%Pt/CeO₂ (HSA), the oxidation of C₃H₈ proceeds through the exothermic direct POX route.

5. Summary and Conclusions

Partial oxidation of hydrocarbons to hydrogen can occur by two sequences of reactions. In one, the indirect sequence, total oxidation to CO₂ and H₂O occurs first, and the secondary reactions produce H₂ further down the reactor. In the direct sequence, partial oxidation to CO and H₂ occurs first, with subsequent (or parallel) conversion to the products of total oxidation.

The complex of reactions involved in partial oxidation of hydrocarbons and the production of hydrogen thereby was modeled by using propane. The catalysts used were 1% Pt/CeO₂ and 1% Ni/CeO₂. The results were consistent with earlier ones [2] obtained with Pt supported on a lower-surface-area ceria obtained commercially.

Matrix-reduction techniques showed that the products observed to be formed experimentally could be attributed to four independent reactions. Based on preliminary experimental observations, ten sets of four reactions were considered plausible. All of these sets contained total oxidation and dehydrogenation, with the balance taken from: partial oxidation, steam reforming, dry reforming, water-gas shift, and water formation.

Experimental data from the reaction of propane with oxygen were used to refine the selection further. Additional experiments were carried out to determine which secondary reactions were plausible under certain outlet conditions.

For the Ni/CeO₂, three sets of independent reactions were found to be equally plausible. The three were very similar, in that they all contained total oxidation, steam reforming and dehydrogenation. The fourth reaction was partial oxidation, dry reforming or water formation. Qualitatively, the same results were found for all four, although some of the details were different. For all three sets, analysis of the experimental data with WHSV (or contact time) indicated that total oxidation is the predominant reaction at all contact times, with steam reforming and/or dry reforming important only at larger contact times. This would correspond to the indirect sequence.

For the Pt/CeO₂, only one set of independent reactions is plausible. This comprises total oxidation, partial oxidation, water formation and dehydrogenation. Analysis of the experimental data with WHSV indicated that total oxidation increases with increasing contact time, while partial oxidation decreases. Hence partial oxidation is most significant at shorter contact times, and the direct sequence would appear to apply here.

The differences observed here 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 would seem to be best for supported platinum catalysts.

Acknowledgments

This study was supported by the U.S. Department of Energy under Cooperative Agreement DE-AC22-99FT40540 with the Consortium for Fossil Fuel Science (CFFS). The sponsor played no role in the study design; collection, analysis and interpretation of data; in the writing of the manuscript; or in the decision to submit it for publication.

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Table I. Sets of possible reactions

Set	Reactions
I	TOX, DH, POX, WGS
II	TOX, DH, POX, SR
III	TOX, DH, POX, DR
IV	TOX, DH, SR, DR
V	TOX, DH, SR, WGS
VI	TOX, DH, POX, WF
VII	TOX, DH, SR, WF
VIII	TOX, DH, DR, WGS
IX	TOX, DH, DR, WF
X	TOX, DH, WGS, WF

Table II. Relations between the rates of independent reactions in Sets I through X (R_j) and formation rates of components (r_i).

Set	$r_{C_3H_8}$	r_{O_2}	r_{H_2}	r_{CO_2}	r_{CO}	$r_{C_3H_6}$
I	$R_{POX} + R_{TOX} + R_{DH}$	$1.5R_{POX} + 5R_{TOX}$	$R_{POX} + R_{WGS} + R_{DH}$	$3R_{TOX} + R_{WGS}$	$3R_{POX} - R_{WGS}$	R_{DH}
II	$R_{POX} + R_{TOX} + R_{SR} + R_{DH}$	$1.5R_{POX} + 5R_{TOX}$	$4R_{POX} + 7R_{SR} + R_{DH}$	$3R_{TOX}$	$3R_{POX} + 3R_{SR}$	R_{DH}
III	$R_{POX} + R_{TOX} + R_{DR} + R_{DH}$	$1.5R_{POX} + 5R_{TOX}$	$4R_{POX} + 4R_{DR} + R_{DH}$	$3R_{TOX} - 3R_{DR}$	$3R_{POX} + 6R_{DR}$	R_{DH}
IV	$R_{SR} + R_{TOX} + R_{DR} + R_{DH}$	$5R_{TOX}$	$7R_{SR} + 4R_{DR} + R_{DH}$	$3R_{TOX} - 3R_{DR}$	$3R_{SR} + 6R_{DR}$	R_{DH}
V	$R_{SR} + R_{TOX} + R_{DH}$	$5R_{TOX}$	$7R_{SR} + R_{WGS} + R_{DH}$	$3R_{TOX} - 3R_{WGS}$	$3R_{SR} - R_{WGS}$	R_{DH}
VI	$R_{POX} + R_{TOX} + R_{DH}$	$1.5R_{POX} + 5R_{TOX} + R_{WF}$	$4R_{POX} - 2R_{WF} + R_{DH}$	$3R_{TOX}$	$3R_{POX}$	R_{DH}
VII	$R_{SR} + R_{TOX} + R_{DH}$	$5R_{TOX} + R_{WF}$	$7R_{SR} - 2R_{WF} + R_{DH}$	$3R_{TOX}$	$3R_{SR}$	R_{DH}
VIII	$R_{DR} + R_{TOX} + R_{DH}$	$5R_{TOX}$	$R_{WGS} + 2R_{DR} + R_{DH}$	$3R_{TOX} + R_{WGS} - 3R_{DR}$	$6R_{DR} - R_{WGS}$	R_{DH}
IX	$R_{DR} + R_{TOX} + R_{DH}$	$5R_{TOX} + R_{WF}$	$2R_{WF} + 4R_{DR} + R_{DH}$	$3R_{TOX} - 3R_{DR}$	$6R_{DR}$	R_{DH}
X	$R_{TOX} + R_{DH}$	$5R_{TOX} + R_{WF}$	$R_{DH} + R_{WGS} - 2R_{WF}$	$3R_{TOX} + R_{WGS}$	$-R_{WGS}$	R_{DH}

Table III. Results for 0.05g 1%Ni/CeO₂ (HSA) catalyst with different inlet volumetric flow rates,

V_{inlet}. Bold face indicates possible sets, as indicated in the text.

Set	V _{inlet}	R _{POX}	R _{TOX}	R _{SR}	R _{DR}	R _{WGS}	R _{WF}	R _{DH}
I	100	0.2561	1.0907			0.2332		0.0137
	200	0.1564	2.2666			0.1981		0.1062
	300	0.1115	3.1291			0.0477		0.1946
	400	0.1003	3.6537			0.0145		0.2837
II	100	0.1266	1.1684	0.1814				0.0137
	200	0.0464	2.3326	0.1541				0.1062
	300	0.085	3.145	0.0371				0.1946
	400	0.0923	3.6586	0.0113				0.2837
III	100	0.3532	1.0324		-0.136			0.0137
	200	0.239	2.2171		-0.1155			0.1062
	300	0.1314	3.1172		-0.0278			0.1946
	400	0.1064	3.6501		-0.0085			0.2837
IV	100		1.2444	0.2826	0.0759			0.0137
	200		2.3605	0.1912	0.0278			0.1062
	300		3.196	0.1051	0.051			0.1946
	400		3.7139	0.0851	0.0554			0.2837
V	100		1.2444	0.3585		-0.2278		0.0137
	200		2.3605	0.219		-0.0835		0.1062
	300		3.196	0.1561		-0.1529		0.1946

	400		3.7139	0.1405		-0.1661		0.2837
VI	100	0.2172	1.1684				-0.272	0.0137
	200	0.1234	2.3326				-0.2311	0.1062
	300	0.1035	3.145				-0.0557	0.1946
	400	0.0979	3.6586				-0.017	0.2837
VII	100		1.1684	0.4345			0.3797	0.0137
	200		2.3326	0.2469			0.1392	0.1062
	300		3.145	0.207			0.2549	0.1946
	400		3.6586	0.1958			0.2768	0.2837
VIII	100		1.2444		0.3585	0.8478		0.0137
	200		2.3605		0.219	0.5736		0.1062
	300		3.196		0.1561	0.3153		0.1946
	400		3.7139		0.1405	0.2554		0.2837
IX	100		1.3857		0.2172		-0.7065	0.0137
	200		2.4561		0.1234		-0.478	0.1062
	300		3.2485		0.1035		-0.2627	0.1946
	400		3.7565		0.0979		-0.2128	0.2837
X	100		1.6029			-1.3034	-1.7926	0.0137
	200		2.5795			-0.7406	-1.0951	0.1062
	300		3.4681			-0.7577	-0.811	0.1946
	400		4.0368			-0.8011	-0.7507	0.2837

Table IV. Results for 0.1 g 1% Ni/CeO₂ (HSA) catalyst with different inlet volumetric flow rates,V_{inlet}. Bold face indicates possible sets, as indicated in the text.

Set	V _{inlet}	R _{POX}	R _{TOX}	R _{SR}	R _{DR}	R _{WGS}	R _{WF}	R _{DH}
I	100	0.6085	0.8657			0.976		0.0453
	200	0.5066	2.172			0.7842		0.0954
	300	0.4149	3.3389			0.5208		0.2014
	400	0.311	4.2782			0.064		0.2543
II	100	0.0663	1.191	0.7591				0.0453
	200	0.0709	2.4334	0.61				0.0954
	300	0.1255	3.5126	0.4051				0.2014
	400	0.2755	4.2996	0.0498				0.2543
III	100	1.0152	0.6217		-0.5693			0.0453
	200	0.8334	1.9759		-0.4575			0.0954
	300	0.6319	3.2087		-0.3038			0.2014
	400	0.3377	4.2622		-0.0373			0.2543
IV	100		1.2308	0.8121	0.0398			0.0453
	200		2.4759	0.6667	0.0425			0.0954
	300		3.5879	0.5055	0.0753			0.2014
	400		4.4649	0.2702	0.1653			0.2543
V	100		1.2308	0.8519		-0.1194		0.0453
	200		2.4759	0.7092		-0.1276		0.0954
	300		3.5879	0.5808		-0.2259		0.2014

	400		4.4649	0.4354		-0.4959		0.2543
VI	100	0.4459	1.191				-1.1386	0.0453
	200	0.3759	2.4334				-0.9149	0.0954
	300	0.3281	3.5126				-0.6076	0.2014
	400	0.3004	4.2996				-0.0747	0.2543
VII	100		1.191	0.8917			0.199	0.0453
	200		2.4334	0.7518			0.2127	0.0954
	300		3.5126	0.6561			0.3766	0.2014
	400		4.2996	0.6007			0.8264	0.2543
VIII	100		1.2308		0.8552	2.4364		0.0453
	200		2.4759		0.7092	2.0001		0.0954
	300		3.5879		0.5808	1.5165		0.2014
	400		4.4649		0.4354	0.8105		0.2543
IX	100		1.6369		0.4459		-2.0304	0.0453
	200		2.8093		0.3759		-1.6667	0.0954
	300		3.8406		0.3281		-1.2638	0.2014
	400		4.5999		0.3004		-0.6754	0.2543
X	100		2.0827			-2.6752	-4.2597	0.0453
	200		3.1851			-2.2553	-3.5462	0.0954
	300		4.1687			-1.9684	-2.9041	0.2014
	400		4.9003			-1.8022	-2.1772	0.2543

Table V. Results for 0.01g 1% Pt/CeO₂ (HSA) catalyst with different inlet volumetric flow rates,V_{inlet}. Bold face indicates possible sets, as indicated in the text.

Set	V _{inlet}	R _{POX}	R _{TOX}	R _{SR}	R _{DR}	R _{WGS}	R _{WF}	R _{DH}
I	100	0.0320	1.2121			-0.3195		0.0159
	200	0.0629	2.3673			-0.6039		0.0469
	300	0.1108	3.4243			-1.0178		0.1161
	400	0.1916	4.3466			-2.0219		0.2131
II	100	0.2096	1.1056	-0.2485				0.0159
	200	0.3984	2.1666	-0.4697				0.0469
	300	0.6762	3.085	-0.7916				0.1161
	400	1.3149	3.6726	-1.5726				0.2131
III	100	-0.1011	1.292		0.1864			0.0159
	200	-0.1888	2.5183		0.3523			0.0469
	300	-0.3133	3.6787		0.5937			0.1161
	400	-0.6509	4.852		1.1794			0.2131
IV	100		1.2313	-0.0809	0.1257			0.0159
	200		2.405	-0.151	0.239			0.0469
	300		3.4907	-0.2507	0.4057			0.1161
	400		4.4615	-0.5207	0.7889			0.2131
V	100		1.2313	0.0448		-0.3772		0.0159
	200		2.405	0.088		-0.717		0.0469
	300		3.4907	0.155		-1.2171		0.1161

	400		4.4615	0.2682	-2.3667		0.2131
VI	100	0.0853	1.1056			0.3728	0.0159
	200	0.1635	2.166			0.7045	0.0469
	300	0.2804	3.085			1.1874	0.1161
	400	0.5286	3.6726			2.3589	0.2131
VII	100		1.1056	0.1706		0.6287	0.0159
	200		2.166	0.327		1.1951	0.0469
	300		3.085	0.5608		2.0286	0.1161
	400		3.6726	1.0571		3.9446	0.2131
VIII	100		1.2313	0.0448	-0.2427		0.0159
	200		2.405	0.088	-0.453		0.0469
	300		3.4907	0.1551	-0.752		0.1161
	400		4.4615	0.2682	-1.5621		0.2131
IX	100		1.1909	0.0853		0.2022	0.0159
	200		2.3295	0.1635		0.3775	0.0469
	300		3.3654	0.2804		0.6266	0.1161
	400		4.2012	0.5286		1.3018	0.2131
X	100		1.2762		-0.5118	-0.2242	0.0159
	200		2.493		-0.981	-0.44	0.0469
	300		3.6458		-1.6823	-0.7753	0.1161
	400		4.7297		-3.1714	-1.3411	0.2131

Table VI. Results for 0.02g 1% Pt/CeO₂ (HSA) catalyst with different inlet volumetric flow rates, V_{inlet} . Bold face indicates possible sets, as indicated in the text.

Set	V_{inlet}	R_{POX}	R_{TOX}	R_{SR}	R_{DR}	R_{WGS}	R_{WF}	R_{DH}
I	100	0.0296	1.2499			-0.2014		0.0201
	200	0.0803	2.4479			-0.6787		0.0545
	300	0.138	3.6261			-1.2565		0.1523
	400	0.2139	4.645			-1.9977		0.2697
II	100	0.1415	1.1827	-0.1567				0.0201
	200	0.4573	2.2217	-0.5279				0.0545
	300	0.8361	3.2073	-0.9773				0.1523
	400	1.3237	3.9791	-1.5538				0.2697
III	100	-0.0543	1.3002		0.1175			0.0201
	200	-0.2025	2.6176		0.3959			0.0545
	300	-0.3855	3.9403		0.733			0.1523
	400	-0.6185	5.1445		1.1653			0.2697
IV	100		1.2677	-0.0434	0.0849			0.0201
	200		2.4961	-0.162	0.2744			0.0545
	300		3.7089	-0.3084	0.5017			0.1523
	400		4.7734	-0.4948	0.7942			0.2697
V	100		1.2677	0.0415		-0.2548		0.0201
	200		2.4961	0.1124		-0.8232		0.0545
	300		3.7089	0.1932		-1.505		0.1523

	400		4.7734	0.2995	-2.3827		0.2697
VI	100	0.0632	1.1827			0.235	0.0201
	200	0.1934	2.2217			0.7918	0.0545
	300	0.3474	3.2073			1.466	0.1523
	400	0.5469	3.9791			2.3307	0.2697
VII	100		1.1827	0.1264		0.4246	0.0201
	200		2.2217	0.3868		1.372	0.0545
	300		3.2073	0.6949		2.5083	0.1523
	400		3.9791	1.0937		3.9712	0.2697
VIII	100		1.2677	0.0415	-0.1303		0.0201
	200		2.4961	0.1124	-0.486		0.0545
	300		3.7089	0.1932	-0.9253		0.1523
	400		4.7734	0.2995	-1.4843		0.2697
IX	100		1.2459	0.0632		0.1086	0.0201
	200		2.4151	0.1934		0.405	0.0545
	300		3.5547	0.3474		0.7711	0.1523
	400		4.526	0.5469		1.237	0.2697
X	100		1.3091		-0.3793	-0.2075	0.0201
	200		2.6085		-1.1604	-0.562	0.0545
	300		3.9022		-2.0846	-0.9661	0.1523
	400		5.0728		-3.2811	-1.4973	0.2697

Table VII. Inlet flow rates for runs testing for secondary reactions. Total inlet flow rate is fixed at 300 sccm; balance is Ar.

Catalyst	Reaction	Feed (sccm)			
		CO	CO ₂	C ₃ H ₈	H ₂ O
0.05g 1%Ni/CeO ₂	DR		8.7	7.5	
0.1g 1%Ni/CeO ₂	DR		9.5	7	
0.05g 1%Ni/CeO ₂	SR			7.5	18
0.1g 1%Ni/CeO ₂	SR			7	18
0.05g 1%Ni/CeO ₂	WGS	0.236			18
0.1g 1%Ni/CeO ₂	WGS	1.27			18
0.01g 1%Pt/CeO ₂	DR		7.5	7.5	
0.02g 1%Pt/CeO ₂	DR		8.5	7.5	
0.01g 1%Pt/CeO ₂	SR			7.5	18
0.02g 1%Pt/CeO ₂	SR			7.5	18

Figure Captions

Figure 1. Effect of total inlet reactant flow rate on outlet flow rate of components over 1%

Ni/CeO₂ catalyst. Catalyst loading, 0.05 g; temperature 300°C, O₂/C₃H₈ = 1.78.

Figure 2. DR activity over 0.05g 1% Ni/CeO₂ (HSA) as a function of temperature. Inlet flow rate as shown in Table VII.

Figure 3. DR activity over 0.1g of 1% Ni/CeO₂ (HSA) as a function of temperature. Inlet flow rate as shown in Table VII.

Figure 4. SR activity over 0.05g of 1% Ni/CeO₂ (HSA) as a function of temperature. Inlet flow rate as shown in Table VII.

Figure 5. SR activity over 0.1g 1% Ni/CeO₂ (HSA) as a function of temperature. Inlet flow rate as shown in Table VII.

Figure 6. DR reactions over 0.01 g of 1% Pt/CeO₂ (HSA) as a function of temperature. Inlet flow rate as shown in Table VII.

Figure 7. DR reactions over 0.02 g of 1% Pt/CeO₂ (HSA) as a function of temperature. Inlet flow rate as shown in Table VII.

Figure 8. Effect of WHSV on modified reaction rates R' of TOX, SR, POX and DH over 1% Ni/CeO₂ (HSA) for Set II.

Figure 9. Effect of WHSV on modified reaction rates R' of TOX, SR, DR and DH over 1% Ni/CeO₂ (HSA) for Set IV.

Figure 10. Effect of WHSV on modified reaction rates R' of TOX, SR, WF and DH over 1% Ni/CeO₂ (HSA) for Set VII.

Figure 11. Effect of WHSV on modified reaction rates R' of POX, TOX, WF and DH over 1% Ni/CeO₂ (HSA) for Set VI.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11