

Sequence of Reactions for Propane Reforming over Pt/CeO₂ Catalysts

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Introduction

The conversion of gasoline to hydrogen is a possible option for fuel-cell feeds, since no infrastructure for hydrogen currently exists. The major technologies for reforming hydrocarbons into hydrogen are catalytic steam reforming (SR), autothermal reforming (AR), and partial oxidation (PO). SR, the commercial process for the production of hydrogen, is carried out at high temperatures and is endothermic. In AR, the heat required for the production of hydrogen by SR can be obtained by total oxidation (TO) which is exothermic. In PO, hydrogen is obtained directly. Of course, in all these processes, all the individual reactions -- SR, PO, TO dry reforming (DR), and water-gas shift (WG) -- occur, but to different extents depending upon process conditions and catalysts. Supported Pt is a common catalyst for all these processes. Ceria has been suggested as a support, due to its high capacity for oxygen and its ability to catalyze WG.

For partial oxidation processes, two sequences of reactions have been proposed: (1) TO of hydrocarbon first (to form CO₂ and H₂O), followed by SR, DR and WG to form H₂; and (2) PO of hydrocarbon first (to form synthesis gas), followed by water formation (WF), dehydrogenation (DH) and other reactions to form CO₂ and H₂O [1]. In this study, we have investigated the sequence of reactions for propane reforming by varying catalyst loadings, flow rates and O₂/C₃H₈ ratios.

Materials and Methods

Two 1.0%Pt/CeO₂ catalysts with supports of different surface areas (SAs) were used for this study. The low-SA ceria was obtained from Aldrich, and the high-SA material was prepared by decomposition of Ce(NO₃)₃·6H₂O. Reactions were carried out in a fixed-bed reactor at 600°C using 90% inert. Of the seven components in the exit stream (CO, H₂, CO₂, H₂O, C₃H₈, C₃H₆ and O₂) all but H₂O were measured independently. Details can be found in Ref. [2].

Results and Discussion

Experimental data on the outlet compositions as functions of catalyst loading and flow rates were analyzed as follows. For the seven components, Gauss Elimination indicates that the minimum number of independent reactions is 4. After elimination of the other possibilities, two such sets of reactions were considered. Set A consists of PO, TO, WF and DH (all other reactions can be "obtained" by combinations of these); Set B consists of PO, TO, WG and DH. Note that there is a net formation of water in Set A, and a net loss in Set B. For each set, a material balance on the six outlet compositions measured allows us to obtain the extents of each of the four reactions in the set. Repeating the procedure for runs under different conditions allows us to determine the effect of catalyst loading, flow rate and surface area on the extent of reactions. Hence the sequence in which these reactions occur can be determined.

For the low-SA catalyst, Set A is a possible sequence of reactions for both loadings. The extents of the four reactions is shown in Figure 1. PO increases with loading and with flow rate, while TO increases with loading and decreases with flow rate. This implies that PO takes place first, as compared to TO. On the other hand, for the high-SA catalyst, Set A is suitable only for the lower loading, while Set B is suitable for the higher loading. However, for all loadings, the relative positions of PO and TO are the same as before: PO first, TO later.

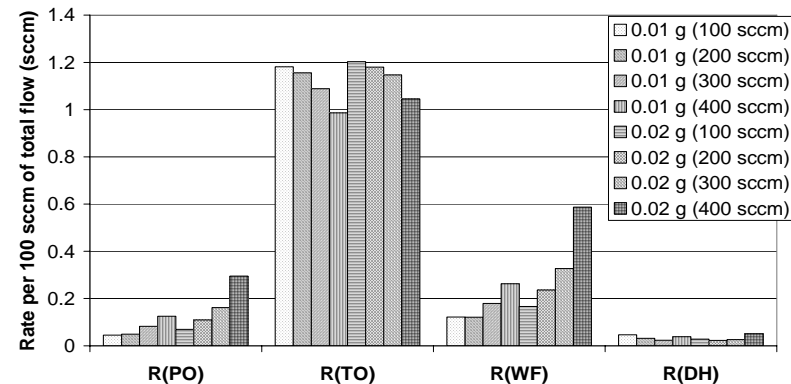


Figure 1. Extent of reaction rates for low-SA catalyst for different flow rates and loadings.

The question of why Set B is required for higher loadings of the high-SA catalyst while Set A is required for the other situations can be answered by looking at the results of changing the O₂/C₃H₈ ratios for the feed. For the higher loading of the high-SA catalyst, Set B is suitable when O₂/C₃H₈ < 3.8 while Set A is suitable when O₂/C₃H₈ > 3.8. In other words, there is sufficient O₂ to form water only when O₂/C₃H₈ > 3.8. For the lower loading of the high-SA catalyst, the shift occurs at O₂/C₃H₈ = 1.5, i.e., there is sufficient O₂ to form water at lower values of O₂/C₃H₈. This is because of the smaller amount of catalyst present, specifically, the CeO₂ support. On the other hand, for the low-SA catalyst, Set A is suitable for all values of O₂/C₃H₈ (at least between 0.5 to 5.0). For this catalyst, even very small amounts of O₂ are sufficient to form water. Clearly the types of products formed (and the types of reactions occurring) depend upon the interactions between the reactants, the support and the noble metal.

Significance

Regardless of the catalyst support, metal loading or reaction conditions used, the sequence of reactions in the autothermal reforming of propane over Pt/CeO₂ consists of partial oxidation first, followed by total oxidation. Depending upon the amount of support CeO₂ present, there may be a net formation of water or a net loss of water.

References

1. Tsang, S.C., Claridge, J.B., Green, M.L.H., *Catal. Today* 23, 3(1995).
2. Bansode, V. MSChE Thesis, West Virginia University, Morgantown WV (2005).