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A comparison of H_2 addition to 3 ms partial oxidation reactions

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Abstract

We compare the effects of adding large amounts of H_2 to 3 ms partial oxidation reactions, ethane to ethylene, propane to olefins, and methane and ammonia to HCN. It is found that H_2 can be safely added at the 2/1 H_2/O_2 stoichiometry in the presence of these fuels without any homogeneous reactions, flames, or explosions. For all of these systems the addition of H_2 increases the selectivities to the desired products while strongly decreasing CO and CO_2. Addition of H_2 forces water formation near the front face of the catalyst which consumes O_2 and allows dehydrogenation processes to dominate. © 2000 Published by Elsevier Science B.V.

Keywords: H_2 addition; Partial oxidation reactions; Dehydrogenation

1. Introduction

It is possible to produce high selectivities of alkanes to partial oxidation products at high conversions with contact times of ∼1 ms by using monolith catalysts without dilution so that the temperatures are close to the adiabatic predictions of ∼1000°C. We have shown [1,2] that CH_4 can be oxidized to produce syngas,

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2,$$

with >90% selectivities at >90% conversion of CH_4.

We have also shown that ethane can be converted into ethylene [3–7] in the reaction

$$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O.$$

We have reported ∼64% selectivity at ∼70% conversion using a Pt catalyst at the 2/1 C_2H_6/O_2 ratio, while ∼68% selectivity at ∼72% conversion was observed using a Pt–Sn catalyst [4].

The oxidative dehydrogenation of propane [8] produces both propylene and ethylene in the overall reactions,

$$C_3H_8 + \tfrac{1}{2}O_2 \rightarrow C_3H_6 + H_2O$$

and

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$

with ∼30% selectivity to each olefin at 50% conversion using a Pt catalyst at the 2/1 C_3H_8/O_2 ratio.

A much older partial oxidation reaction is the ammoxidation of CH_4 with NH_3 to produce HCN [9,10],

$$CH_4 + NH_3 + O_2 \rightarrow HCN + 2H_2O + H_2,$$

which has been carried out commercially for ∼40 years over Pt–10% Rh gauze catalysts.

We have recently reported that addition of large amounts of H_2 to the ethane oxidation process combined with use of Pt–Sn catalysts produces much higher selectivities of ethylene [6,7]. The ethylene selectivity rises to ∼82% at ∼72% conversion of C_2H_6, the CO falls from ∼20 to ∼5%, and the CO_2 becomes negligible.

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In this paper, we compare addition of H_2 to these three reaction systems.

2. Experimental

Apparatus and procedures have been described in detail previously [1–5]. Experiments were carried out in 18 mm diameter quartz tubes with monolith catalysts sealed into them with alumina cloth. For olefins the catalyst was α-alumina foam with ∼80% void fraction onto which was impregnated ∼5% Pt and Sn by depositing concentrated salt solutions and drying. For HCN synthesis the catalyst was five layers of 40 mesh Pt–10% Rh gauze.

Feed flow rates were controlled with mass flow controllers at reactor pressures of ∼1.2 atm and total flow rates of ∼5 SLPM for superficial velocities in the reactor of ∼1 m/s. At the typical 1000°C of the catalyst the linear velocities were 3–10 m/s for residence times between 0.5 and 5 ms. We used high purity gases without dilution except that we typically added 30% N_2 for calibration of the gas chromatograph. Catalysts were ignited by heating with a Bunsen flame while flowing at the desired composition; when the catalyst began to glow, the flame was removed, and insulation was added to attain nearly adiabatic temperatures.

Hydrogen was added to the fuel and O_2 mixture after the catalyst was ignited. Also, H_2 was removed first when the reactor was shut down. With these precautions, we observed no flames or explosions in these systems for H_2/O_2 from 0 to at least 3/1. While we found no literature that stated that these mixtures are not flammable, the addition of large amounts of alkane fuel to the 2/1 H_2/O_2 mixture evidently suppresses homogeneous reaction by making the system extremely fuel rich and producing hydrocarbon radical species which scavenge the radical species that propagate the flame.

3. Ethane to ethylene

Fig. 1 shows C_2H_6 conversion and the selectivities to various products vs. the C_2H_6/O_2 ratio without H_2 added in the feed. Selectivities are calculated on a C atom basis. The O_2 conversion was >99% for all experiments. The temperature of the catalyst decreased with increasing C_2H_6/O_2 ratio and was ∼950°C at the 2/1 ratio, which was within 50° of the calculated adiabatic temperature for these products for feed at 25°C. It is seen that selectivity to ethylene increases with C_2H_6/O_2 while the ethane conversion decreases. At 2/1, the ethylene selectivity is 68% using the Pt–Sn catalyst compared to 64% using Pt alone, and the conversion is ∼2% higher on Pt–Sn.

However, adding H_2 causes a large increase in ethylene selectivity, as shown in Fig. 2. With Pt alone the selectivity rises from 64 to 72% while with Pt–Sn the selectivity increased from 68 to 82% for H_2/O_2=2/1. Up to H_2/O_2=1 on Pt, the selectivity increases with no corresponding change in conversion. Beyond H_2/O_2=1 on Pt, the conversion decreases with no corresponding change in selectivity. With Pt–Sn, conversion actually increases slightly for small amounts of H_2 and is almost the same at the 2/1 ratio as with no H_2 added.

The major effect of adding H_2 is a decrease in CO and CO_2 selectivities which fall from 17 to 5% and 6 to <1%, respectively, at the 2/1 H_2/O_2 ratio on Pt–Sn.

4. Propane to olefins

While the partial oxidation of ethane primarily yields ethylene, the partial oxidation of propane yields both propylene and ethylene. Fig. 3 shows the C_3H_8 conversion and selectivities to various products as a function of the C_3H_8/O_2 ratio using a Pt catalyst. Interestingly, the selectivities to ethylene and propylene are nearly equivalent at C_3H_8/O_2=2/1. The total olefin selectivity of ∼65% is comparable to the ethylene selectivity in ethane partial oxidation on the same Pt catalyst. Also, the adiabatic temperatures are approximately 950°C, which are similar to ethane partial oxidation temperatures. However, the fuel and oxygen conversions are well below those in ethane partial oxidation. One possible explanation for the lower conversion is the fact that propane has three carbon atoms. While the alkane/O_2 ratios are the same for both experiments, the carbon atom to oxygen atom ratio is larger for propane.

Fig. 4 shows the effects of adding hydrogen to C_3H_8/O_2=2/1 using a Pt catalyst. Up to H_2/O_2=1/1, the total olefin selectivity increases while the C_3H_8 conversion remains nearly constant. Above

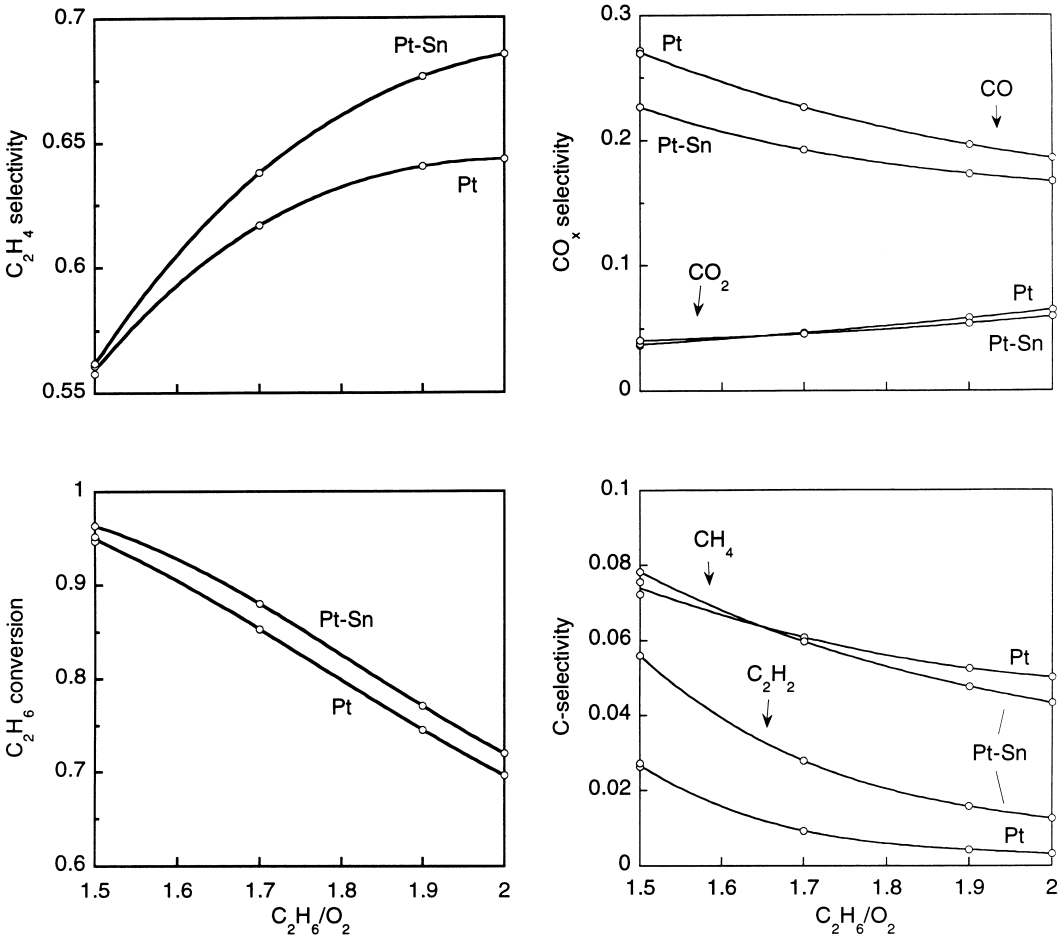

Fig. 1. Plot of conversion of C_2H_6 and selectivities to various products vs. C_2H_6/O_2 ratio for partial oxidation of ethane over Pt and Pt–Sn catalysts on α-alumina foams with no H_2 added in the feed. At the 2/1 stoichiometric ratio Pt produces 64% selectivity to C_2H_4 at 70% C_2H_6 conversion, while Pt–Sn produces 68% selectivity at 72% conversion. Other carbon containing products are CO, CO_2, and C_2H_2. All other species had selectivities less than 1%.

H_2/O_2=1/1, the total olefin selectivity remains constant while the C_3H_8 conversion decreases. Again, we see the total olefin selectivity of ∼75% is comparable to the ethylene selectivity in ethane partial oxidation while the fuel and oxygen conversions are much lower. Hydrogen addition decreases the CO and CO_2 selectivities from 8 to 5% and 11 to 3%, respectively at H_2/O_2=2/1.

With Pt–Sn catalysts the selectivities and conversion are increased with propane similar to results shown in Fig. 2, except for the loss in olefin selectivity caused by CH_4 formation associated with ethylene. These results will be discussed in a later publication.

5. Methane and ammonia to HCN

For HCN synthesis from CH_4, NH_3, and O_2, we used a 1/1 CH_4/NH_3 mixture and added O_2, with results shown in the left panels of Fig. 5. The upper panel shows the conversion of NH_3 and the selectivity based on NH_3 (the N atom selectivity), while the lower panel shows the conversion of CH_4 and the selectivity based on CH_4 (the C atom selectivity). Also plotted in the figure is the per pass yield *Y*, which is the selectivity multiplied by the conversion. It is seen that there is a maximum in yields and the selectivities become independent of composition near $(CH_4+NH_3)/O_2$=2.

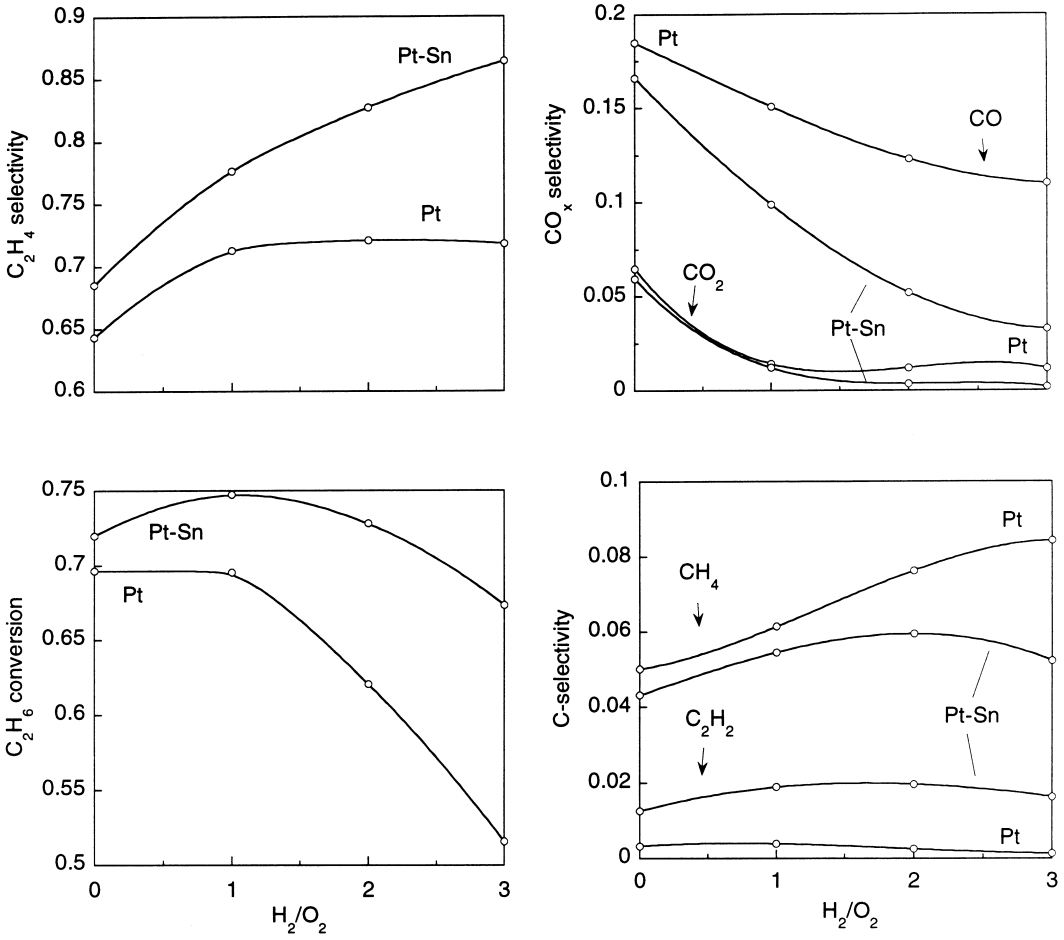

Fig. 2. Plot of conversion of C_2H_6 and selectivities to various products vs. H_2/O_2 ratio for C_2H_6/O_2=2/1 for partial oxidation of ethane over Pt and Pt–Sn catalysts on α-alumina.

The right panels of Fig. 5 show the effect of H_2 addition at the 1/1/1 feed ratio of the left panels. It is seen that the conversion and selectivity based on CH_4 is nearly independent of H_2 added. However, the selectivity based on NH_3 increases strongly with H_2 addition from 72% without H_2 to 82% for H_2/O_2=0.8. The selectivity increase could be related to the conversion decrease.

The conversion of NH_3 falls with H_2 addition such that the yield decreases. However, in HCN production the unreacted NH_3 is usually recycled (so that the overall yield is equal to the selectivity), so that the increased selectivity upon addition of H_2 may be beneficial.

6. Discussion

6.1. Mechanism

We have discussed the mechanisms of these processes in detail previously [11–15]. We have also simulated these reactions using models of methane to syngas, partial oxidation of ethane and ammoxidation of methane on Rh and Pt surfaces. We have used one-dimensional and two-dimensional models to simulate these processes including variable transport coefficients and including heat and mass transfer effects in explaining these results. We have also examined extensively the role of homogeneous processes

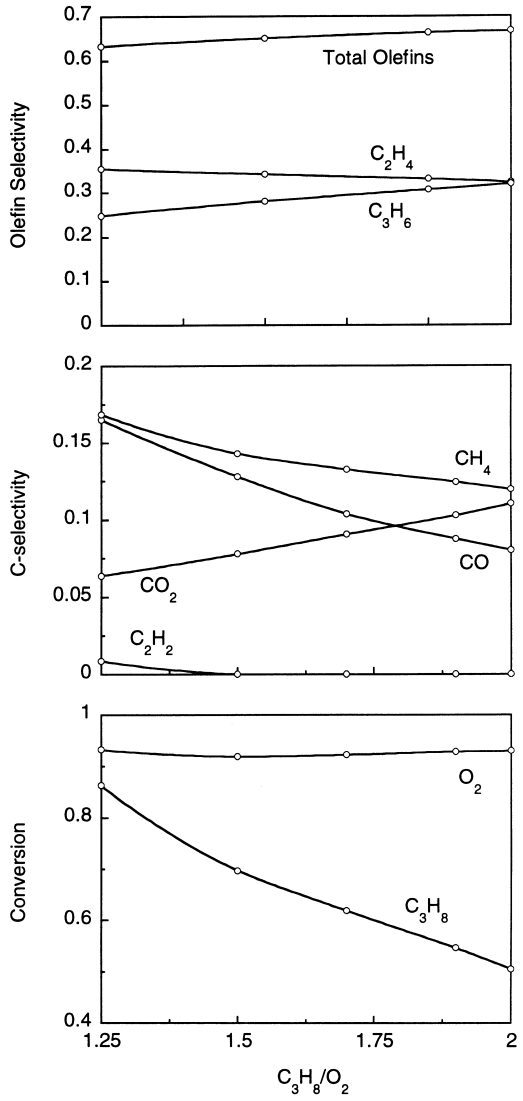

Fig. 3. Plot of conversion of C_3H_8 and selectivities to various products vs. C_3H_8/O_2 ratio over a Pt catalyst. The total selectivity to olefins is ~65% and the ethylene and propylene are approximately equal.

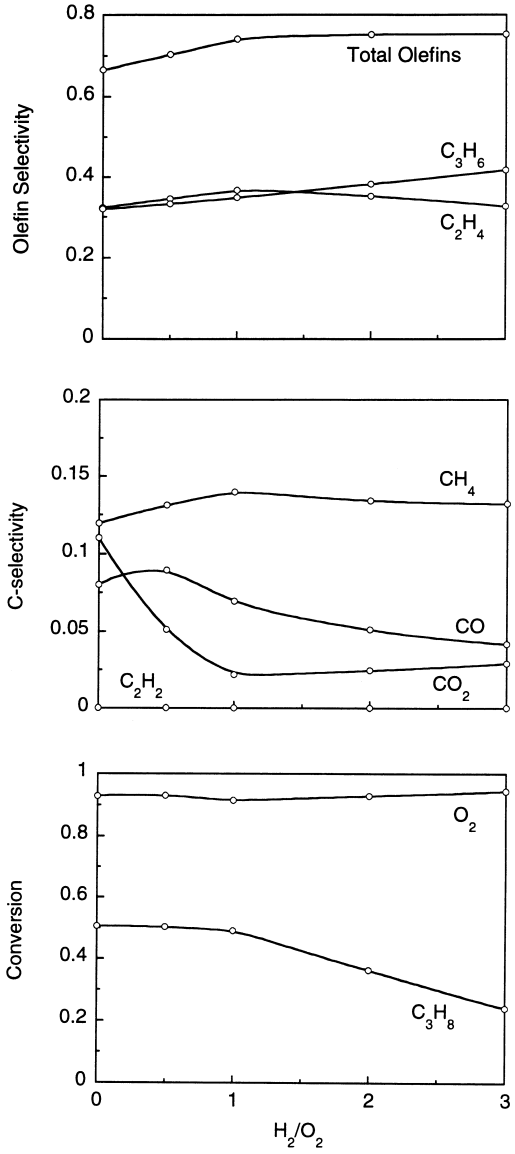

Fig. 4. Plot of conversion of C_3H_8 and selectivities to various products vs. H_2/O_2 ratio for C_3H_8/O_2=2/1 on a Pt catalyst. The total selectivity to olefins increases to ~75% and more propylene is produced than ethylene.

in these reaction systems. We find that methane to syngas and to HCN occur primarily by surface reactions with little contribution of homogeneous reaction steps. However with ethane and higher hydrocarbons the alkanes are more reactive and some homogeneous reaction may occur, although its exact contribution is yet to be decided.

Basically, all of these processes occur by the direct reactions yielding the products observed. That is, the products are formed by the adsorption of the parent alkanes and their subsequent reactions on the surface to produce the observed species in a small number of rapid elementary steps. Some olefins may be formed by direct dehydrogenation in the gas phase, although

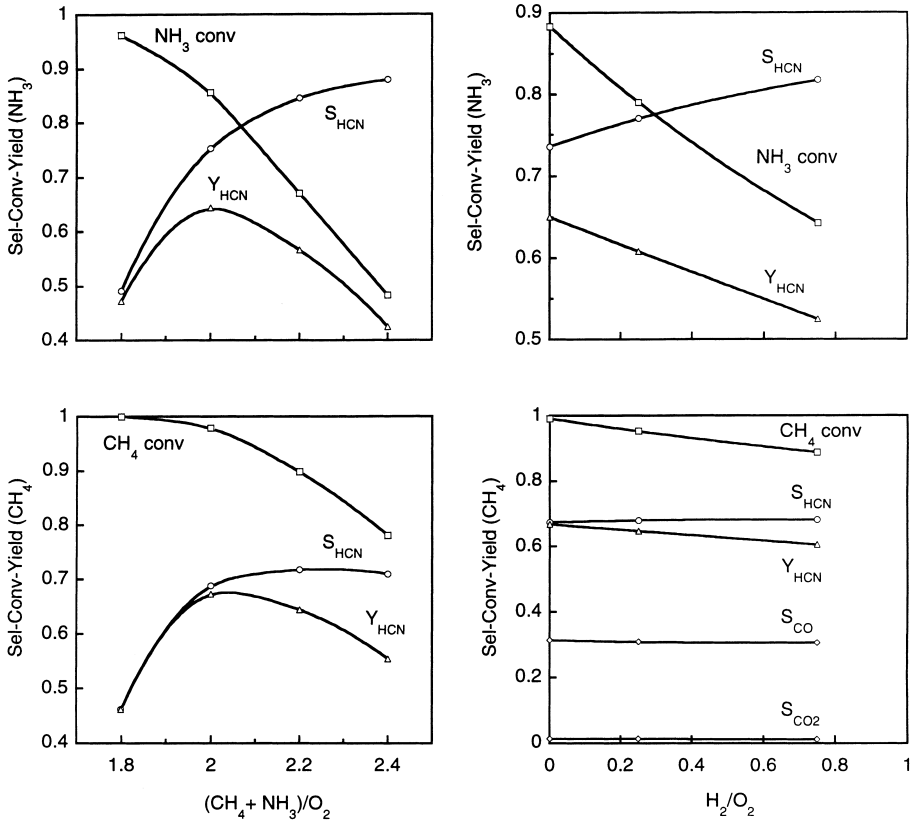

Fig. 5. Left panels show plots of CH_4 and NH_3 conversions and selectivities to various products vs. $(CH_4+NH_3)/O_2$ without H_2 addition. The right panels show selectivities and conversions vs. H_2/O_2. The selectivity to HCN based on NH_3 rises with addition of H_2 while the NH_3 conversion decreases. H_2 addition does not strongly affect the conversion or selectivity based on CH4.

different catalysts produce quite different product distributions.

For all of these reactions the major products are not those predicted by chemical equilibrium which predicts less than 1% olefins or HCN for these feed conditions and temperatures. Equilibrium predicts mostly CO, CH_4, and considerable carbon in the form of graphite. Short contact time reactors clearly produce mostly single products at yields far from thermodynamic equilibrium.

In this paper, we focus on the role of H_2 in increasing the selectivities to the desired products while suppressing deep oxidation to CO and CO_2. This occurs because addition of H_2 rapidly consumes O_2, thus suppressing oxidation of the alkanes. Heat is gained from the rapid H_2+O_2 reaction, while heat is lost from the suppression of the fuel$+O_2 \rightarrow CO_x$ reactions. The net effect is a temperature change of less than 50°C.

Hydrogen successfully competes with alkanes for adsorption because the sticking coefficients of H_2 are higher than those of alkanes. Probably more important, the diffusion coefficient of H_2 is much higher than that of the higher molecular weight alkanes. Since all of these reactions are mass transfer limited, this gives a large preference for H_2 oxidation compared to alkane oxidation.

The H_2 oxidation reaction is exclusively catalytic and produces H_2O near the front face of the catalyst. The heat from the H_2+O_2 reaction generates the heat necessary to drive the dehydrogenation processes quickly. We believe the H_2+O_2 reaction is entirely heterogeneous for a few reasons. First, the reactants are flowing into the front face of the catalyst at room temperature. Second, large amounts of alkanes are known to effectively suppress homogeneous chemistry; in fuel rich reactions, alkanes are good radical

scavengers. Third, we never see visible flames or explosions.

7. Hydrogen consumption and production

These reactions generate H_2 as a product of dehydrogenation of the alkanes and NH_3. As shown in Fig. 6, when no H_2 is added in the feed (the left side of the horizontal axis) ethane oxidation produces ~0.9 H_2 per mole of O_2 fed to the reactor, propane produces only 0.2 mol of H_2, and HCN produces ~1.3 mol of H_2 per mole of O_2 fed to the reactor.

When H_2 is fed to the reactor, one expects that more H_2 might appear in the products, and the dashed lines in Fig. 6 indicate the amount of H_2 that would be produced is all of the H_2 fed appeared in the product.

These processes would probably not be commercially viable if large amounts of H_2 had to be imported into the processes because H_2 is costly to produce (by converting methane to syngas). However, all of the alkane fuels contain hydrogen, and therefore the processes can produce H_2 in amounts comparable to that fed into the reactor. The solid curves in Fig. 6 are the moles of H_2 produced per mole of O_2 fed into the reactor. If this curve is above the H_2 fed into the reactor (dashed lines), then the process is a net producer of H_2, and no additional H_2 may be needed if the H_2 produced can be separated and recycled into the reactor.

As seen in Fig. 6, for ethane to ethylene the process produces more H_2 than fed for $H_2/O_2 < 2$ on Pt and $H_2/O_2 < 1.75$ on Pt–Sn. For propane to olefins, the process never produces excess H_2 beyond $H_2/O_2 = 0.1$. For HCN the process produces more H_2 than fed for $H_2/O_2 < 1.5$. The crossover points depend strongly on process conditions such as the fuel to oxygen ratio and preheat. We conclude that for C_2H_4 and HCN synthesis it is easy to attain feed and process conditions where the process produces more H_2 than fed into the reactor.

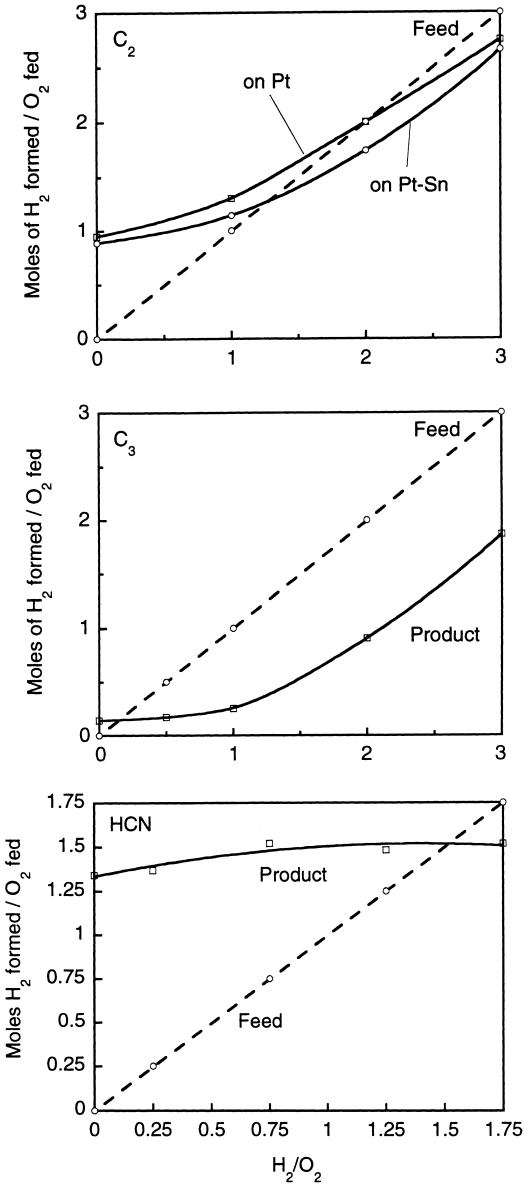

Fig. 6. Moles of H_2 produced per mole of O_2 fed (vertical axis) vs. the moles of H_2 fed per mole of O_2 fed into the reactor (horizontal axes). The dashed lines are the situation where the reaction produces as much H_2 as is fed. When the curves are above the dashed lines, the process should be a net producer of H_2 if H_2 is recycled and fed back into the reactor.

8. Summary

Addition of large amounts of H_2 to these partial oxidation processes in very short contact time reactors can give significant increases in selectivities to the desired products. This occurs because H_2 reacts very quickly with O_2 near the front face of the catalyst to produce H_2O which generates the heat necessary to drive the reaction quickly. This reaction also removes O_2 from the system to suppress oxidation to CO and

CO_2 which allows the desired dehydrogenation process to dominate.

These processes can also generate as much H_2 as is fed to the reactor so that, with recycling, no additional H_2 need be imported into the process in a commercial process.

While addition of H_2 to any oxidation process may be thought to be dangerous, it is in fact inflammable over wide ranges of feed compositions, catalysts, and temperatures (for the experiments we have tried). Millisecond reactors provide extreme conditions where some reactions are very rapid and the products go to compositions that are far from equilibrium. Chemical processes under extreme conditions may have many other possible reactions and conditions where desired chemicals can be produced both efficiently and economically.

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