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On-line addition of catalyst in high-temperature reactors: high selectivity to olefins [*]

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By adding solutions containing catalyst salts to hot monolith catalysts during partial oxidation processes, the salt decomposes instantly and is deposited selectively near the front face. We have used this technique to deposit extremely small amounts of Pt on α-Al_2O_3 monoliths during ethane oxidation to olefins. We find that on this catalyst with H_2 addition, the selectivity to ethylene rises from ∼65 to over 80% at an ethane conversion of ∼60% and at complete O_2 conversion. We also examine the addition of promoters including Sn, which gives improved performance compared to the Pt catalyst alone. This appears to be a general effect that could be useful in preparing catalysts with different loadings and distributions in high-temperature processes. It can also be used for rapid and accurate diagnosis of catalysts and additives and to modify catalysts on-line in situations where deactivation or catalyst loss occurs.

Keywords: Pt/Al_2O_3 catalyst, on-line Pt addition, high-temperature reactor, catalyst promoters, catalytic performance, ethane oxidation

1. Introduction

We have recently shown that addition of hydrogen in the oxidative dehydrogenation of ethane produces an increase in the selectivity to ethylene from 70 to over 85% using a Pt–Sn catalyst prepared on α-alumina monolith support [1–3]. In contrast, for Pt alone without Sn, the selectivity with H_2 addition rises only from 65 to 72%. We interpret these results as indicating that the Pt–Sn surface causes the selective H_2 oxidation reaction

$$H_2 + (1/2)O_2 \rightarrow H_2O$$

which reduces the deep oxidation of ethane

$$C_2H_6 + O_2 \rightarrow 2CO + 3H_2$$

to allow its dehydrogenation

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

to predominate. We also found that the H_2 produced is comparable to the H_2 fed so that with H_2 separation and feedback, the process does not require additional H_2.

In this paper, we show that Pt alone gives considerable enhancement of olefin selectivity if the Pt is added on-line from a solution to a hot monolith support, allowing the high reaction temperature to decompose the Pt salt rapidly and depositing Pt selectively near the front face in very small quantities. Upon adding H_2, the C_2H_4 selectivity increased from ∼65 to over 80% using such a Pt catalyst prepared on-line as compared to only ∼72% using a Pt catalyst prepared using conventional deposition methods.

This technique can also be used to restore lost activity of the Pt–Sn bimetallic catalyst by adding Sn and compensating for the metal lost due to evaporation. It can also be used to rapidly screen various catalyst metals or promoters for such high-temperature catalytic reactions.

2. Experimental

Normal catalysts were prepared by dripping an aqueous solution of hexachloroplatinic acid uniformly on to the support, which typically consisted of a 92% α-Al_2O_3 foam monolith with $\sim 1/2$ mm pore diameter or 45 pores per inch (ppi), 18 mm external diameter and 10 mm length. The catalyst was allowed to dry overnight after which the salt was decomposed by heating in a furnace at 600 °C for several hours.

To prepare catalysts on-line and run partial oxidation experiments, an apparatus as shown in figure 1 was used. A foam monolith was wrapped in alumina paper and placed inside an 18 mm diameter quartz reactor. A solution typically containing ∼10 mg H_2PtCl_6 dissolved in ∼1 ml distilled water was sucked into a syringe attached to a 4 inch hypodermic needle. This needle was passed through a rubber septum secured in the upstream end-cap so that its tip was just above the front face of the upper monolith. The needle could be moved laterally to allow deposition over the entire surface of the monolith.

Reaction gases passing through mass flow controllers were premixed and passed through the reactor. For preparation, a fresh alumina foam was sealed into the reactor. A few drops of the Pt-salt solution were uniformly dripped over the front face and the foam was externally heated using a Bunsen burner up to ∼350–400 °C. The solution dried off after a few minutes and the front face turned black in

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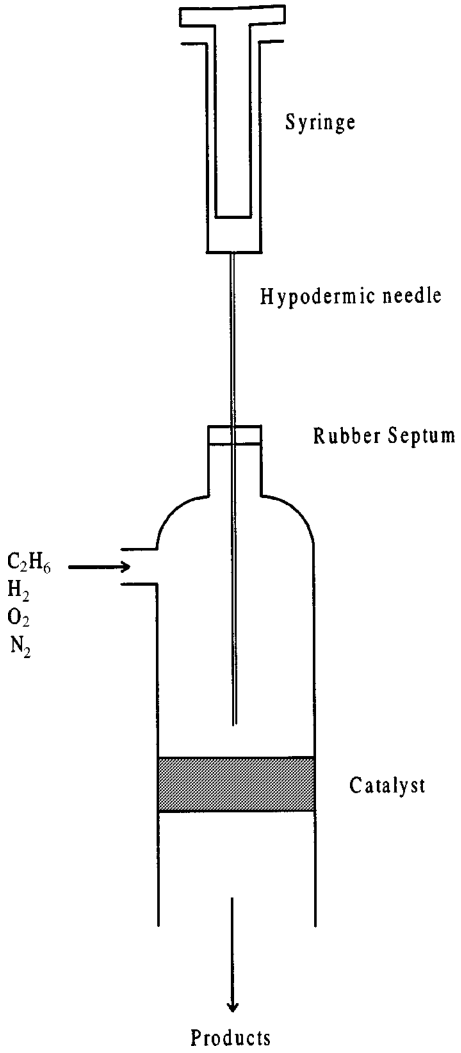


Figure 1. Experimental apparatus used for on-line addition of catalyst salts to a partial oxidation reaction. A hypodermic needle connected to a syringe is passed through a rubber septum and placed on top of the catalyst operating at ∼1000 °C. Controlled quantities of the desired catalyst or promoter can be deposited selectively on the front face using this technique.

color indicating that the salt had decomposed to Pt metal. This was followed by ignition at a random glowing spot on the front face, which immediately propagated throughout the surface. The burner was then removed and the reaction zone was insulated to achieve nearly adiabatic conditions.

Product gases were analyzed using gas chromatography. Nitrogen (30%) was used as a calibration standard since it is inert in the reaction. Up to C_4 species were analyzed, and C, H and O balances always closed to within 5%.

3. Results

3.1. On-line catalysts

Figure 2 compares experimental results obtained on a conventional, uniformly coated Pt and Pt–Sn catalyst to a Pt catalyst prepared on-line. The weight loading of Pt on the conventional Pt and Pt–Sn catalyst was ∼1% (∼0.02 g of Pt on ∼2 g Al_2O_3 foam monolith) and the Sn/Pt ratio on the Pt–Sn catalyst was ∼3/1. To prepare the on-line catalyst, ∼0.04 g of H_2PtCl_6 was dissolved in 5 ml distilled water and sucked into a syringe. Approximately 0.5 ml of this solution was dripped uniformly on the front surface. This corresponds to only 2 mg of Pt for an overall Pt loading of <0.1% on the on-line catalyst based on the total weight of the support.

Results are plotted as a function of the H_2/O_2 ratio. The C_2H_6/O_2 ratio was maintained at 2/1, total flow rate was 5 slpm and the outlet pressure was 1.2 atm. The nitrogen dilution was 30%. H_2 was added in appropriate amounts holding other flow rates constant. Hence total flow rate increased and nitrogen dilution decreased with H_2 addition.

On the uniformly coated Pt catalyst, the C_2H_4 selectivity increased from 65 to 72% and the C_2H_6 conversion decreased from 70 to ∼52% upon adding H_2. The C_2H_4 selectivity increased from 65 to 70% and conversion remained constant up to $H_2/O_2 \approx 1$. Beyond this ratio, further H_2 addition decreased C_2H_6 conversion with a slight increase in C_2H_4 selectivity. On the other hand, on the uniformly coated Pt–Sn catalyst, the C_2H_4 selectivity increased from 65 to ∼87% with H_2 addition while C_2H_6 conversion remained around 70%.

Equilibrium calculations predict that addition of H_2 to the C_2H_6–O_2 feed mixture leads to a negligible improvement in olefin selectivity and no effect on C_2H_6 conversion [1]. Hence, experimental trends in selectivities and conversions on both the uniformly coated and on-line Pt catalysts do not agree well with those predicted if the product gases approach equilibrium, which indicates that the experimental conversions and selectivities are controlled primarily by the kinetic and not thermodynamic considerations.

On the Pt catalyst prepared on-line, C_2H_4 selectivity increased continuously with H_2 addition, rising from ∼65 to 85% similar to that on the Pt–Sn catalyst. The drop in conversion was also much lower than that on the uniform Pt catalyst. At $C_2H_6/O_2/H_2 = 2/1/2$, the on-line Pt catalyst gave 81% C_2H_4 selectivity at 63% conversion, compared to 72% selectivity at 62% conversion on the Pt catalyst. CO and CO_2 selectivities decreased and CH_4 selectivity increased on both Pt catalysts with H_2 addition, but the decrease in CO, CO_2 was faster and the increase in CH_4 was slower on the on-line catalyst. Hence we see a considerable difference in selectivities obtained from these catalysts although they are both essentially Pt catalysts on Al_2O_3 supports.

Results with various H_2/O_2 and C_2H_6/O_2 ratios using the uniformly coated Pt and Pt–Sn catalysts are compared to those using the on-line Pt catalyst in figure 3, which is plotted as C_2H_4 selectivity versus C_2H_6 conversion. Solid curves represent varying C_2H_6/O_2 ratios while the dashed curves represent results with varying H_2/O_2 ratio at $C_2H_6/O_2 = 2$. We see that the on-line catalyst gives considerably higher C_2H_4 selectivity with H_2 addition compared

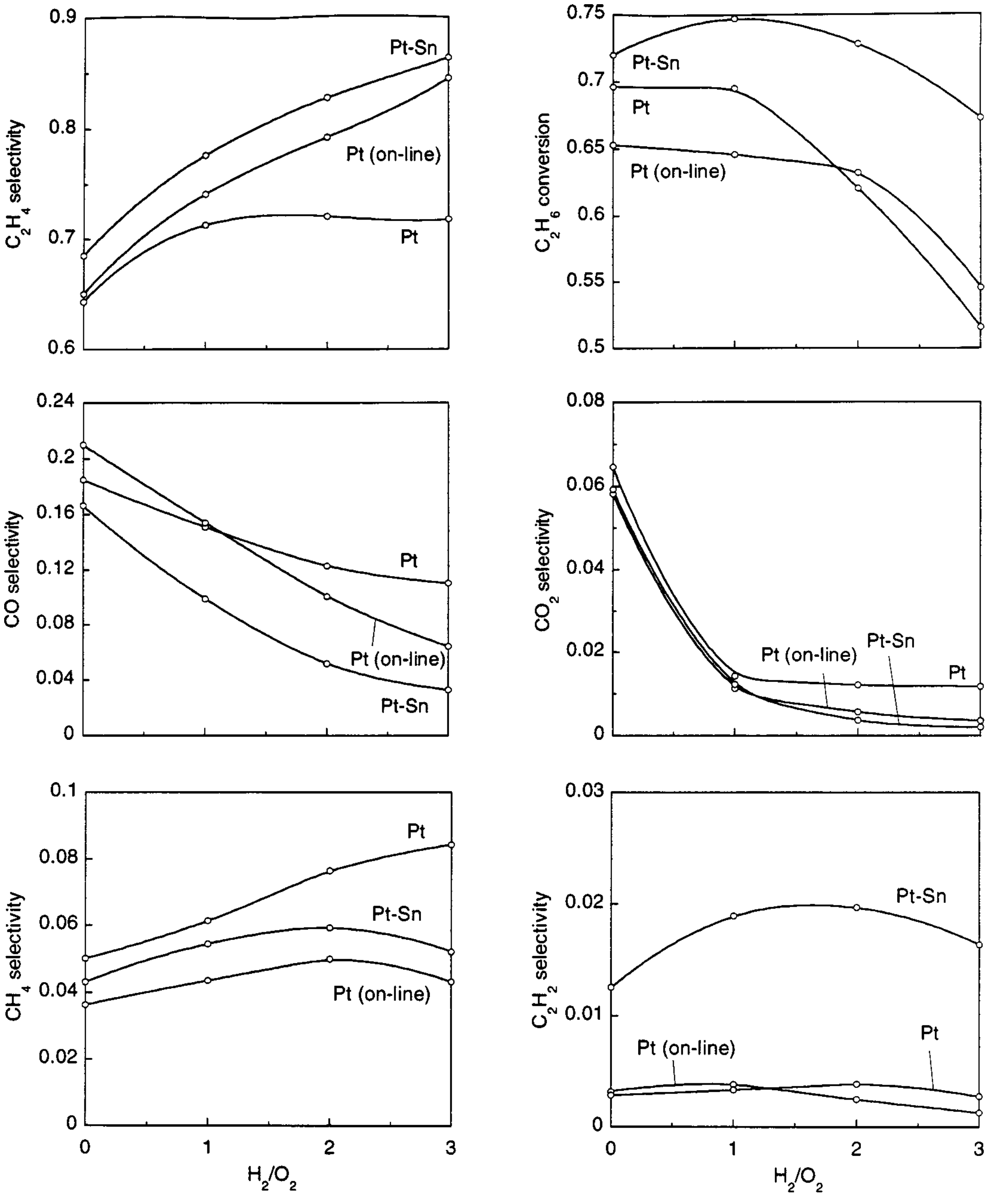


Figure 2. Comparison of a Pt catalyst prepared on-line by dripping an aqueous H_2PtCl_6 solution on to a hot α-Al_2O_3 monolith to Pt/α-Al_2O_3 and Pt–Sn/α-Al_2O_3 catalysts prepared using the conventional wetting technique. Plots are selectivities and conversion as a function of H_2/O_2, at $C_2H_6/O_2 = 2$. The Pt catalyst prepared on-line gives higher C_2H_4 selectivity and lower CO, CO_2 and CH_4 selectivities than the conventional Pt catalyst.

to the uniform catalyst. The increase in C_2H_4 selectivity with H_2 addition on this catalyst is almost comparable to that on the Pt–Sn catalyst, although the conversion is much lower.

3.2. On-line regeneration

At $C_2H_6/O_2/H_2 = 2/1/2$, a fresh Pt–Sn catalyst gives 84% selectivity to C_2H_4 at 68% C_2H_6 conversion. This performance is at least comparable to that of a steam cracker, making the oxidative dehydrogenation process a promising alternative process for ethylene reactors. However, as the Pt–Sn catalyst loses Sn due to its high vapor pressure at reaction temperature of ~1000 °C, its activity deteriorates with time on-stream. The selectivity and conversion drop from 84 to 81% and from 68 to 61%, respectively, over a period of 24 h. To maximize the production of ethylene, it is crucial that the lost activity of the Pt–Sn catalyst be restored. Figure 4 shows application of the on-line addition technique to regenerate this lost activity. 0.08 g of $SnCl_2$ was dissolved in 8 ml distilled water and after 24 h of operation, ~0.5 ml (around 20–30 drops) of this solution was added over the entire front face of the deactivated catalyst. This led to an increase in the selectivity

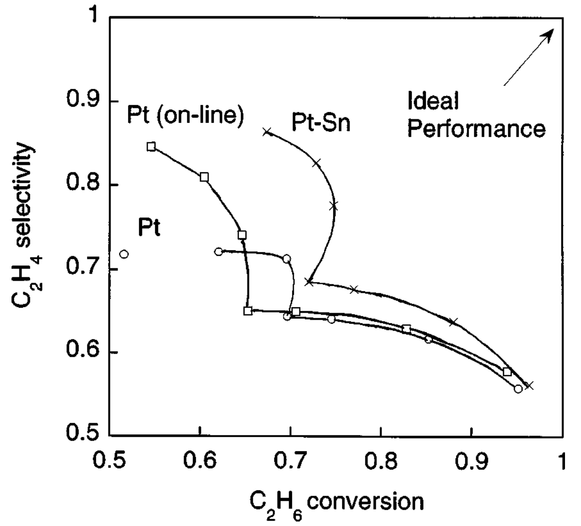


Figure 3. $S_{C_2H_4}$ versus $X_{C_2H_6}$ for Pt/α-Al_2O_3 and on-line Pt catalysts. Solid curves represent experiments with varying C_2H_6/O_2 ratios while dashed curves represent experiments at $C_2H_6/O_2 = 2$ with varying H_2/O_2 ratios. The Pt catalyst prepared on-line gives considerably higher C_2H_4 selectivity with H_2 addition compared to that prepared using conventional techniques. Also plotted are results obtained on Pt–Sn/α-Al_2O_3 catalyst for comparison sake.

and conversion from 81 and 61% to 83.5 and 66%, respectively.

3.3. On-line addition of promoters

Figure 5 illustrates the application of the on-line deposition technique to screen multiple catalyst and promoter metals in a single experiment. The experiment was initially run at a C_2H_6/O_2 ratio of 2/1 and no H_2 addition with a Pt catalyst prepared on-line. This gave ~65% selectivity at 68% conversion, consistent with results in figure 2. Upon addition of Sn, the selectivity and conversion increased by ~5 and 3%, respectively. H_2 was then added to this Pt–Sn catalyst prepared on-line with $H_2/O_2 = 2/1$, resulting in ~86% selectivity at 64% conversion. Additional amounts of Pt and Sn were also added after some time. In general, C_2H_4 selectivity rose and C_2H_6 conversion fell upon adding Pt, and both selectivity and conversion increased upon adding Sn to the catalyst. Finally, a few drops of Cu were added, which resulted in a slight decrease in the C_2H_4 selectivity and ~8% increase in C_2H_6 conversion. In a similar manner, we have tried addition of various other promoter metals on-line to a Pt catalyst to investigate their

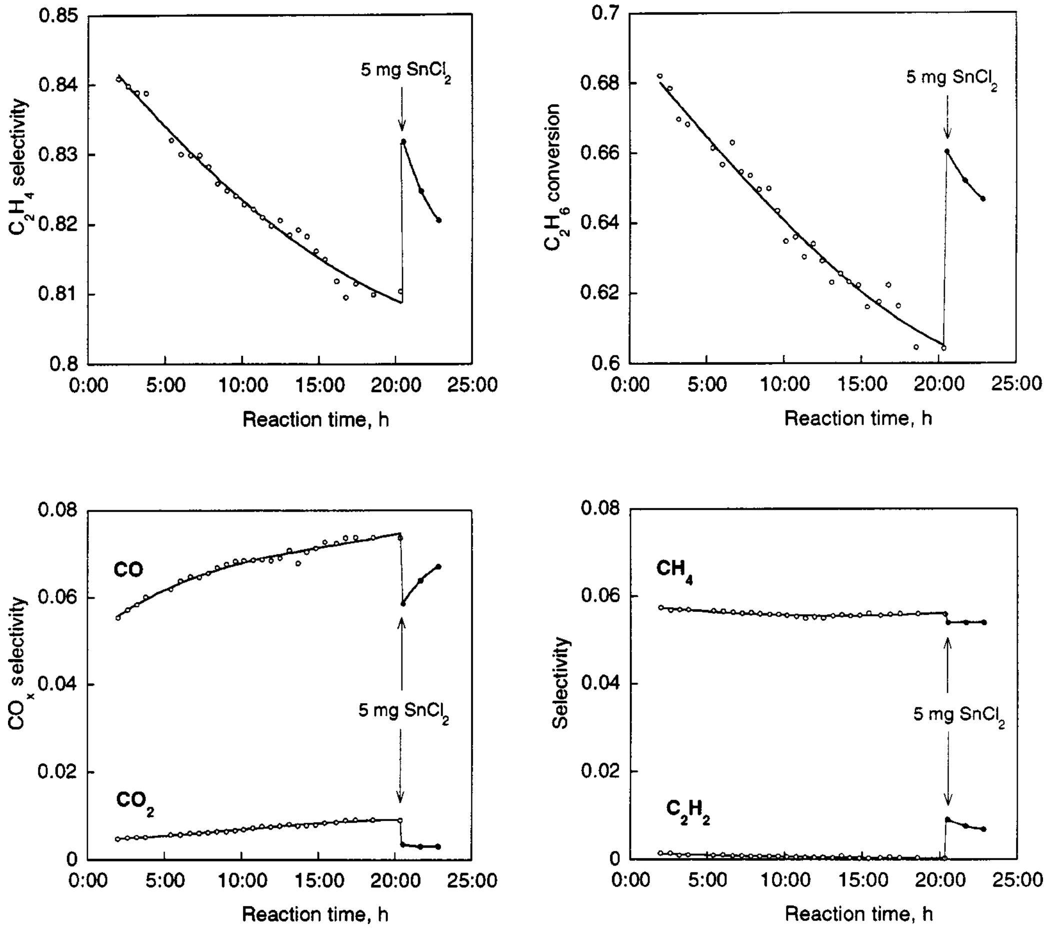


Figure 4. Regeneration Pt–Sn catalyst using the on-line addition technique. C_2H_4 selectivity and C_2H_6 conversion drop by ~3 and 8% over 20 h of operation, after which 0.1 g $SnCl_2$ is dissolved in 8 ml H_2O and ~0.4 ml of this solution is uniformly dripped on the front face of the catalyst using the on-line addition technique. Selectivity and conversion are seen to recover by 2.5 and 6% by addition of only 5 mg $SnCl_2$.

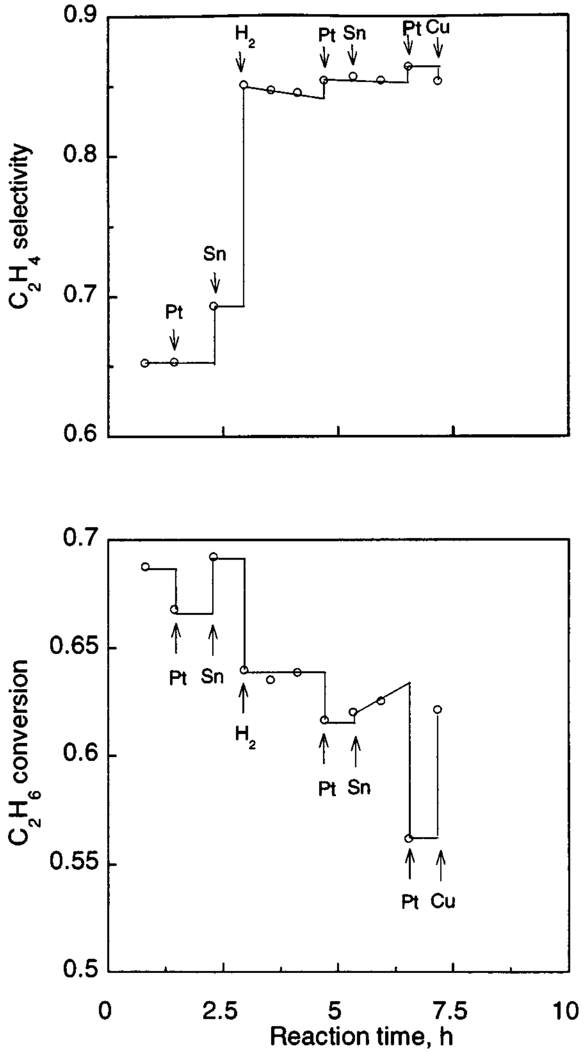
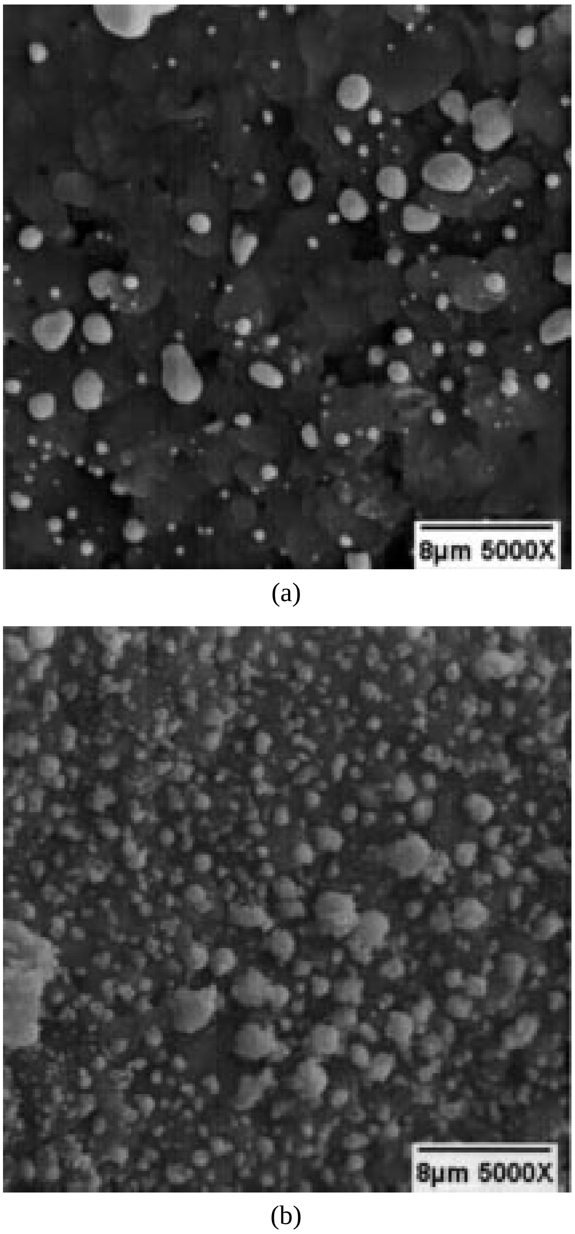


Figure 5. Continuous on-line addition of metal salts on to a Pt catalyst operating at ∼1000 °C. Graphs are variations in C_2H_4 selectivity and C_2H_6 conversion with addition of Pt, Sn and Cu salts in minute quantities. The experiment is run at $C_2/O_2/H_2 = 2/1/0$ for the first 2.5 h and at 2/1/2 after 2.5 h. The on-line addition technique can be used to quickly screen catalysts and/or promoter metals for catalytic reactions in a single experiment.

effect on selectivities and conversion. Of additives examined, only Sn, Cu and Ag showed improved performance compared to Pt alone.

3.4. Surface analysis

We characterized these catalysts using SEM and XRD techniques. Figure 6 shows scanning electron microscope images at a magnification of 5000× of a uniformly coated Pt/α-Al_2O_3 catalyst (panel (a)) and one that is prepared on-line (panel (b)). The support surface in both catalysts is uniformly covered by roughly spherical, micron sized, crystalline Pt particles. While the Pt particles on the conventional Pt catalyst are very smooth, the surface of the Pt particles on the on-line catalyst is very rough. This roughness must be because the Pt salt decomposes immediately upon contacting the hot monolith surface, which leads to many small Pt crystals adhering together. On the other hand, the Pt salt is coated much more uniformly on the conventional Pt catalyst leading to formation of mostly single Pt catalysts. In both situations, average particle size was ∼1 μm. We will report more detailed catalyst characterization experiments in a later publication [4].



(a)

(b)

Figure 6. SEM images of Pt catalysts at 5000×. Panel (a) shows the front surface of a Pt/α-Al_2O_3 catalyst prepared by the conventional wetting technique. The support is covered uniformly by micron sized, crystalline FCC Pt particles with smooth surfaces. Panel (b) shows the surface of a Pt/α-Al_2O_3 catalyst prepared on-line. Although the particle size is comparable to that in panel (a), the surface is considerably rougher.

4. Discussion

We have shown that H_2 addition to Pt/α-Al_2O_3 increases C_2H_4 selectivity only from 65 to ∼72%. However, when

H_2 is added to a Pt catalyst prepared on-line, C_2H_4 selectivity increases from 65 to over 80% indicating that the performance of the Pt-coated catalyst is considerably affected by its preparation technique.

The effect of method of preparation on catalytic reaction systems has of course been studied extensively. As examples, Chang et al. [5] reported the dependence of selectivity of cyclohexanol dehydrogenation on the method of preparation of Cu/α-Al_2O_3 catalysts. The selectivity to cyclohexanone increased as the Cu loading increased up to a certain limit, and then decreased as the loading increased further for catalysts prepared by impregnation. Jin [6] reported that the performance of a platinum–tin catalyst for dehydrogenation of long chain alkanes was significantly dependent on the method of preparation. Hicks et al. [7] illustrated the effect of dispersion and crystallite size on the activity of supported Pt catalysts for methane and heptane oxidation. Huang et al. [8] demonstrated the effect of catalyst preparation and loading on the performance of a Ni/γ-Al_2O_3 catalyst for steady-state CO hydrogenation. Jovanovic et al. [9] reported the influence of method of preparation of a Ni/mullite catalyst on the high-temperature oxidation of propane to CO and H_2. There have been several investigations on the influence of preparation and arrangement of Pt/Rh gauze packs on catalytic behavior for nitric acid and hydrogen cyanide synthesis [10,11].

The on-line Pt/α-Al_2O_3 catalyst has a much lower total Pt loading than uniformly coated Pt/α-Al_2O_3, typically $\sim$2 mg of Pt deposited near the front surface of the Al_2O_3 ceramic support weighing $\sim$2 g, versus 20 mg or higher for the uniformly coated Pt catalyst. We previously investigated the effect of Pt loading in this reaction [12]. Upon decreasing the Pt weight loading from 5 to <1%, C_2H_4 selectivity and conversion increased only by $\sim$1–2% while it increased by $\sim$10% on the on-line catalyst. Therefore, lower Pt loading must not be the only cause for improved performance of the on-line catalyst. The selective deposition of Pt near the front surface must result in shorter contact times with the Pt particles on the catalyst, and this could also be important. However, to explain the effect of contact time on catalyst performance, it is important to first understand the mechanism of the overall process. While details remain to be elucidated, we summarize some features below.

The reaction occurs at very short contact times of the order of milliseconds and at high temperatures near 1000 °C, conditions very different from most catalytic processes. While Pt/α-Al_2O_3 gave 65% C_2H_4 selectivity and 70% conversion at $C_2H_6/O_2 = 2$, $\sim$25% formed oxidation products such as CO and CO_2, $\sim$5% formed CH_4 and 5% formed higher hydrocarbons such as C_3H_6 and C_4H_8. Upon adding H_2 to the feed, CO and CO_2 selectivity decreased continually from 25 to 12%. This suggests that the process operates in two distinct steps as suggested in figure 7. In the first step occurring near the front surface of the catalyst, C_2H_6 and H_2 react with O_2 to form oxidation products such as CO, CO_2 and H_2O. These exothermic reactions then drive the subsequent endothermic dehydrogenation of C_2H_6 to C_2H_4 in the second step. Temperatures upstream and downstream of the catalyst were experimentally measured to be within $\sim$100 °C of each other. This, however, does not eliminate the possibility of a variable axial temperature profile inside the catalyst, as represented in figure 7(d), corresponding to highly exothermic oxidation reactions, although we observe only small variations experimentally. The extent of sequential endothermic dehydrogenation reactions could be strongly dependent on the temperature profile and the contact time with the surface of the catalyst, and these should probably take place mostly in absence of oxygen in the later part of the catalyst, as shown.

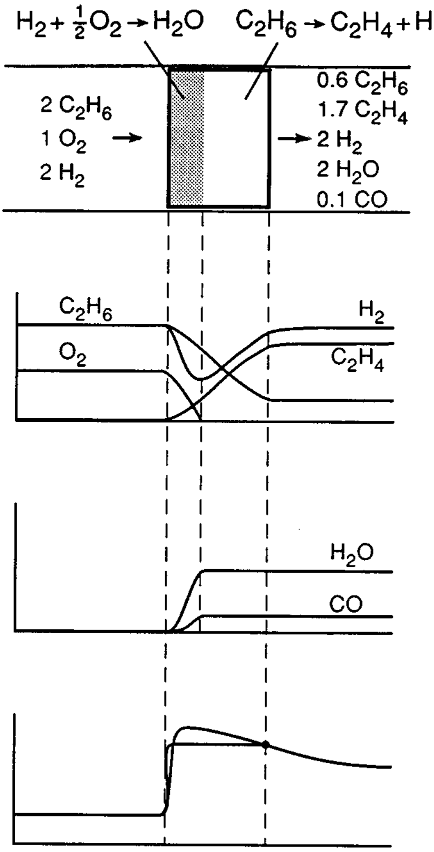


Figure 7. The two-zone reaction model for Pt/α-Al_2O_3 catalyst for oxidative dehydrogenation. Oxidation of H_2 and C_2H_6 occurs in the first part of the catalyst and consumes O_2 very quickly. This is followed by the dehydrogenation reactions of C_2H_6 to produce C_2H_4, CH_4 and higher hydrocarbons. Although temperatures upstream and downstream of the catalyst are experimentally observed to be within $\sim$50–100 °C, the possibility of a temperature spike corresponding to exothermic reactions cannot be eliminated.

In the early part of the catalyst with significant amount of O_2 in the gas phase, surface characterization experiments coupled with one-dimensional modeling calculations indicate that the Pt surface should be predominantly oxygen covered [13]. C_2H_6 and H_2 should dissociatively adsorb on the surface and react with the O-radicals to form OH and CO, which can react further to form CO_2. Most of the O_2 is predicted to react rapidly within few molecular layers of Pt after which the catalyst surface should become O-deficient. Under these conditions, β-elimination of an H atom from the absorbed C_2H_5 radicals should result in formation of C_2H_4 which should rapidly desorb. Alternatively C_2H_4 could further react to form C_2H_2 and C radicals eventually forming CH_4 and higher hydrocarbons such as C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}.

4.1. H_2 addition to Pt and Pt–Sn catalysts

H_2 addition to Pt/α-Al_2O_3 should increase the coverage of surface H atoms, producing more H_2O in the earlier part and more CH_4 in the later part of the reactor. This should increase the C_2H_4 selectivity due to reduction in the formation of CO and CO_2. This prediction is consistent with our experimental results on the Pt catalyst, as C_2H_4 and CH_4 selectivities increased from 65 to 70% and from 5 to 8%, respectively, and CO_x selectivity decreased from 25 to 12% with H_2 addition.

Higher C_2H_4 selectivities were observed on Pt–Sn catalysts compared to Pt, especially with H_2 addition ($\sim$11% greater C_2H_4 selectivity at $C_2H_6/O_2/H_2 = 2/1/2$). This was a direct consequence of reduced CO, CO_2 selectivities ($\sim$8% at 2/1/2), and partly because of reduced formation of CH_4 and higher hydrocarbons ($\sim$3% at 2/1/2) [1] on the Pt–Sn catalyst.

4.2. On-line Pt and Pt–Sn catalysts

On-line deposition technique deposits catalyst metals in extremely small quantities (<0.1% by weight) selectively on the front surface of the monolith support and must result in much smaller contact time of the gas phase with the Pt on the catalyst. Since O_2 is completely converted, the Pt loading on the on-line catalyst must be sufficient to catalyze oxidation reactions of H_2 and C_2H_6. Since considerable amounts of C_2H_4 are observed in the product, the Pt loading must also be sufficient for the dehydrogenation of C_2H_6 to C_2H_4. This suggests that the remaining part of the uniformly coated Pt catalyst predominantly contributes to further reactions of C_2H_4 to form undesired by-products. Since most of this downstream Pt coated section is absent in the on-line catalyst, the improvement in C_2H_4 selectivity on this catalyst must be mainly because of reduction in the formation of by-products such as CH_4, C_2H_4 and other hydrocarbons by subsequent C_2H_4 reactions, and not due to reduction in the CO, CO_2 selectivity as in the case of a Pt–Sn catalyst. Experimental results (figure 2) show that an on-line Pt catalyst gives $\sim$9% higher C_2H_4 selectivity at $C_2H_6/O_2/H_2 = 2/1/2$. As shown in figure 2, only $\sim$3% of this improvement is due to reduction in CO, CO_2 selectivity while $\sim$6% is due to reduction in CH_4 $\sim$3%, C_2H_2, C_3H_6 (1%), C_3H_8 (1%) and other hydrocarbons ($\sim$1%), which is consistent with the above argument.

Therefore, although both Pt–Sn and on-line Pt catalysts give considerably higher C_2H_4 selectivity than a Pt catalyst, these catalysts seem to operate by different mechanisms. Addition of Sn to Pt increases the rate of H_2 oxidation compared to C_2H_6 oxidation and reduces the selectivity to CO and CO_2. On the other hand, on-line Pt catalyst provides an order of magnitude lesser Pt surface in the axial direction, and prevents further reactions of C_2H_4 to undesired hydrocarbons.

These arguments suggest that a Pt–Sn catalyst prepared by depositing both Pt and Sn on-line would combine the preferential $H_2 + O_2$ reaction with minimization of unwanted C_2H_4 reactions. Experiments with Pt–Sn catalysts prepared using on-line deposition techniques give $\sim$2–3% higher selectivity to C_2H_4 compared to a uniformly coated Pt–Sn catalyst. However the difference between Pt–Sn/α-Al_2O_3 and on-line Pt–Sn/α-Al_2O_3 catalysts is not as large as the difference between Pt and on-line Pt catalysts.

4.3. Homogeneous chemistry

Homogeneous ethane and hydrogen oxidation reactions occur with comparable rates, and simulations of gas-phase reactions predict only minor improvements in ethylene selectivity by hydrogen addition [1,2]. These calculations were performed using Mims–Dean and GRI mechanisms containing $\sim$450 chemical reactions and $\sim$115 chemical species [14,15]. This suggests that the oxidation reactions must primarily occur on the Pt surface. We previously suggested two possible mechanisms to explain these experimental results: (i) both oxidation and dehydrogenation reactions occur on the surface of the Pt-based catalyst, as discussed earlier in this section; (ii) the exothermic reaction occurs on the catalyst surface which increases the gas-phase temperature and leads to homogeneous dehydrogenation of ethane to ethylene.

We simulated the purely homogeneous pyrolysis of ethane using the Mims–Dean mechanism assuming only gas-phase reactions at a constant temperature of 950 °C, and calculated selectivities and conversions as a function of the residence time [1]. This pyrolysis calculation predicts very high selectivities to ethylene (>90%), but the conversion of ethane depends strongly on the residence time, and increases from 10% at a residence time of 0.1 ms to 95% at 50 ms. The reaction time required to obtain 70% ethane conversion is $\sim$10–20 ms, which is an order of magnitude longer than that required in these experiments. Furthermore, because of shorter catalyst residence times in an on-line catalyst than a completely coated Pt catalyst, homogeneous pyrolysis simulations predict that an on-line catalyst should give $\sim$15–20% lower ethane conversion and only 2–3% higher ethylene selectivity. This does not agree well with experimental results since an on-line Pt catalyst gives much greater ethylene selectivity than Pt/α-Al_2O_3 at comparable conversions. Therefore, trends in conversions and time scales for the coupled heterogeneous–homogeneous mechanism appear to differ considerably between theory and experiment.

5. Summary

We have shown that for oxidative dehydrogenation of ethane with hydrogen addition, it is possible to obtain over 80% C_2H_4 selectivity at $\sim$60% C_2H_6 and $>$99% O_2 conversions using Pt alone on α-Al_2O_3 support if the Pt is deposited on-line onto the hot alumina monolith. Under such conditions, the catalyst salt decomposes rapidly to Pt metal and is deposited in extremely small quantities near the front face of the support. A catalyst prepared by depositing Pt uniformly by using impregnation techniques gives only $\sim$72% C_2H_4 selectivity. We have also shown the applicability of this on-line deposition technique to rapidly screen various catalyst metals and promoters in a single experiment, and to regenerate catalysts *in situ* by adding metal directly on a glowing catalyst inside an operating reactor.

The improvement in performance of the on-line Pt catalyst compared to the uniformly coated Pt catalyst is because of reduced reactions of C_2H_4 to undesired by-products such as CH_4 and other hydrocarbons and not because of decreased selectivity to CO and CO_2 as in the case of the Pt–Sn catalyst. Further experiments and models will be required to determine the detailed mechanisms of these processes.

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