

Superior Pt-alloy catalysts for oxidative dehydrogenation of ethane to ethylene in microchannel reactors

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Introduction

Ethylene is an important intermediate in the production of many chemicals, but most especially plastics. Today ethylene is produced in the petrochemicals industry via steam cracking. In this process, gaseous or light liquid hydrocarbons are briefly heated to 750–950 °C, causing numerous free radical reactions to take place. Generally, in the course of these reactions, large hydrocarbons break down into smaller ones and saturated hydrocarbons become unsaturated.

High temperature catalytic oxidative dehydrogenation (ODH) of ethane to ethylene is an alternative to steam cracking that has been under study for the past several years. High ethylene yields have been reported at short contact times using Pt monolithic catalysts. Addition of hydrogen in the feed gas has been reported to improve selectivity. Despite these results, efforts to obtain ethylene yields higher than that for steam cracking have been elusive.

Velocys, Inc. in collaboration with The Dow Chemical Company and Pacific Northwest National Laboratory and under the sponsorship of the U.S. Department of Energy's Industrial Technology Program, have explored the catalytic selective ODH of ethane through the use of a high-intensity, heat integrated microchannel reactor. The potential benefits for such a process design, in combination with new catalyst technology, are improved feedstock utilization and substantial energy savings through improved control of the reaction temperature and enhanced catalyst activity and selectivity.

Experimental

The catalysts were synthesized by coating Pt and other metals on coupons with an α - Al_2O_3 layer. The catalysts were heat-treated at 900 °C in flowing H_2 prior to testing. The single channel test reactor has two microchannels separated by a catalyst coupon. Reactants were fed at 3:2:1 ratio of ethane:hydrogen:oxygen. Catalyst entrance temperature ranged from 800 to 950°C. The contact time was fixed at 40 ms. Reaction products, e.g., CO, CO_2 , and C1-C4 hydrocarbons, were analyzed with an on-line four-column GC. Fresh catalysts were characterized by SEM/EDS, XPS and surface XRD analyses.

Results and Discussion

Utilizing microchannel reactors that minimize peak temperatures by effectively distributing and removing heat, we have investigated a series of Pt-alloy catalysts for the ODH of ethane to ethylene. Catalysts studied include Pt-Sn, Pt-Cu and other Pt-metal alloys, directly coated on metal coupons with an α - Al_2O_3 layer. Under the previously described reaction conditions, ethylene selectivities and yields exceeded 83 and 67%, respectively. In comparison, steam cracking reactors commonly provide an ethylene selectivity of 85% and yield of 55%. In addition, catalyst performance was stable for 80-120 hours time on stream.

One Pt-alloy catalyst was also tested in a multi-channel device with a higher output capacity. The device was operated at a 4:6:1 ethane:hydrogen:oxygen ratio and total flow rate of 10 SLPM. The device was operated for more than 120 hours at high ethane conversion and high ethylene selectivity. During the operating window, the ethane conversion exceeded 75% and the ethylene selectivity exceeded 82% (Fig. 1). In addition, during operation the pressure drop remained steady at less than 4 psi.

Some Pt-alloy catalysts (e.g., Pt-Cu) were characterized by surface XRD, SEM/EDS and XPS analyses. One coupon was coated with Pt and Cu and analyzed without any further treatment. A second Pt-Cu coated coupon was heat treated at 900 °C for 4 hours in flowing H_2 . A third Pt-Cu coated coupon was calcined at 900 °C for 4 hours in air after the H_2 heat treatment. For the untreated Pt-Cu coated coupon, only Pt and Cu metal phases were seen. The surface was fully covered with nano-size Cu metal particles. After the heat-treatment in H_2 , the Pt and Cu particles sintered and formed a Pt-Cu solid solution and Cu_3Pt alloy. Both Pt (18 mol%) and Cu (82 mol%) were seen at the surface, suggesting Pt and Cu inter-diffusion at high temperatures. After calcination in air, Cu was oxidized to CuO. The surface was covered with micron-size CuO, while the Pt was still in metallic form underneath. Based on the above characterization results, it is concluded that CuO is present on the surface in the front of Pt-Cu catalyst bed, where O_2 is present. With O_2 consumption, the second zone becomes a reducing atmosphere, where the Cu_3Pt alloy is present.

Significance

This work offers improved feedstock utilization, energy savings and environmental benefits.

Figure 1. Oxidative dehydration of ethane to ethylene in a microchannel device

