

Chemical Kinetics of Ethane Oxidation and Methane Oxidation with Platinum

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Abstract

This particular experiment focuses on the chemical kinetics of catalyst-driven ethane oxidation and methane oxidation and aims at opening up a new field for study among different types of catalysts and their effective applications to society.

Introduction

Shock tubes have been used to study the chemical kinetics of applications ranging from combustion to biomedical research. They are often used to determine reaction rate data for homogeneous reactions and provide mechanistic information for various reactions, but never for heterogeneous systems. The main feature of using the shock tube is for its capability to rapidly raise the temperature and pressure to reacting conditions and drop back to its original conditions almost as rapidly. This application is similar to that of a unit step function (analogous to switching something on and off) and has the ability to freeze the reaction with the intermediates in time, thus allowing for reactions with defined periods of time. In addition, the shock tube method disregards any effects that fluid dynamics may have on the content.

In short, a shock tube creates a shock wave that causes a drastic increase to reacting temperatures, allowing for the content of the shock tube to react until the cooling wave quenches the reaction as ambient conditions are restored. A shock wave is a wave that travels faster than the speed of sound in a given medium. To generate a shock wave, the shock tube consists of a high-pressure driver section and a low-pressure driven section separated by a diaphragm. (ADD FIGURE) As soon as the diaphragm bursts, the large pressure difference causes the production of a shock wave that propagates down the shock tube faster than the speed of sound within its medium where it collides with the end-wall and bounces back. This causes a nearly instantaneous jump in pressure and temperature. As the shockwave bounces back it collides with the contact surface which is the interface that separates the driver and driven section that travels at a lower velocity than the shock wave. This collision causes an additional jolt in pressure and temperature instantaneously, and results in the creation of region 5. At the same time a shock wave is produced, a rarefaction wave concurrently starts traveling in the opposite direction of the shock wave and will be reflected off of the back wall. The rarefaction wave then travels down the shock tube and reaches region 5, acting as a cooling wave that brings the

temperature and pressure back to its initial conditions and therefore quenching the reaction.

The goal of this experiment is to study the chemical kinetics of catalytic reactions. Catalysts increase the rate of chemical reaction without being consumed during the process of the reaction. Because catalyzed reactions have lower activation energies than non-catalyzed reactions, this allows for a higher rate of reaction at the same temperature, which can be very beneficial in real-world applications, ranging from fighting the increased production of greenhouse gases to addressing several of modern society's problems in energy demand. There have not been any experiments involving catalysts within shock tubes before.

In this experiment, a short contact time substrate (SCT) will be used. SCT reactors are currently used in industry for a variety of applications, from fuel cell reformers and chemical synthesis. Effectively, the SCT is a ferralloy (a special kind of stainless steel) wire mesh coated with a catalytic element. In this experiment, the coated element is platinum on gamma-alumina.

With the addition of the catalyst, we expect to see less of the initial reactants in a shock run with a catalyst as opposed to a shock run without a catalyst. This is due to the qualities of a catalyst, which includes further driving a reaction towards completion. The goal of this experiment is to implement effective ways to work with catalysts in shock tubes.

Experimental Methods

For this project, all experiments were done using 4 bar shocks at temperatures varying from 900 to 1600 K in a low pressure shock tube. The low pressure shock tube was designed to operate at relatively low pressures (1-15 bar) allowing for its contents to react at high temperatures (1000-1500 K). The setup of the low pressure shock tube requires two thin films each of 1 mm and 2 mm thickness as diaphragms. A gas chromatograph (GC) was used to analyze the intermediates produced during each experiment.

The driver gas was comprised of a combination of Helium and Argon, depending on the desired reacting temperature and reaction time. Various reaction times from 1.6 to 6.1 ms were tested to determine if the reaction time had an effect on the difference seen between the thermal and catalytic reactions.

Test mixtures of Ethane or Methane and oxygen were diluted in argon and used as the driven gas. The concentration of ethane and methane varied from 100 to 1000 ppm with stoichiometric oxygen concentrations. Different fuels and fuel concentrations were tested to determine if this promoted a change between the thermal and catalytic reactions.

Short contact time elements (SCT) coated with a platinum on gamma-alumina catalyst were used for each catalytic experiment. The SCT was inserted in the end-wall so it resided within Region 5. The number of SCTs at the end-wall varied from 1 to about 15

to determine the optimal amount of SCTs so that there was no interference with the shock.

Results and Discussion

Effects of reaction time

The first test mixture chosen to be tested for this set of experiments was a 100ppm concentration of ethane combined with oxygen at stoichiometric ratio diluted with argon. Ethane was chosen because it is easily oxidized. It was hypothesized that a fuel that oxidizes at low temperatures would show a significant increase in reaction with the addition of a catalyst. When the shocks were run at 4 bar and between 900-1600 K with and without the catalyst, the results were compared and no significant changes were observed.

A possible cause for not detecting a significant difference was that the catalyst surface was not given enough time to heat up to the temperature of the gas. By increasing the concentration of argon in the driver gas, the overall driver gas density increased, causing an increase in reaction time. This is because a higher density fluid takes longer to propagate through the shock tube. (See figure 2)

These shocks were repeated with a higher reaction time of 5.9 to 6.1 ms. Comparing the reactions without catalyst, an increase in reaction time causes an increase in reaction. This can be seen in Figure blah. The same results were seen when comparing the catalytic reactions. However, the increased reaction time did not distinguish the catalyst-driven reaction from the thermal-driven reaction.

Effects of reactant concentration

An increase of concentration of ethane from 100 to 500 ppm was implemented to the test mixture. The experiments done with test mixture were done at temperatures varying from blah to blah K at 5.9-6.1 ms. A higher concentration of reactants was thought to magnify the difference between the reactions with and without catalyst, however there was no significant change.

It was hypothesized that inserting extra SCT's would magnify the conversion due to the extra surface area of catalyst, which presents the test mixture with more opportunities to interact with the catalyst. Experiments were run with both 100 and 500 ppm ethane at temperatures of 900 to 1200 K and a reaction time between 5.9 and 6.1 ms with about 15 SCTs placed at the endwall. The opposite effect was seen where an increase in the amount of catalyst cause at significant decrease in reaction. This was most likely due to the large amount of SCTs interfering with the shock.

Effects of fuel

Methane is more difficult to oxidize than ethane, so it was hypothesized that adding a catalyst would cause a significant change in reaction at low temperatures. Experiments were run using 1000 ppm methane at temperatures between 1000 and 1100 K at reaction times of about 5.9-6.1 ms with and without catalyst. These results showed no significant difference between thermal and catalytic methane oxidation reactions.

A different GC that measured other compounds of interest, such as CO₂, was available to analyze the products for three experiments. Figure 6 shows the concentration of CO₂ as a function of temperature measured for those experiments. These results indicate a trend that the addition of a catalyst causes an increase in CO₂ production and therefore an increase in reaction. Placing an additional SCT (two SCTs total) at the end-wall also showed an increase in CO₂ production proving that an increase in the amount of catalyst causes an increase in reaction. Since only one experiment for each case was performed and the change in CO₂ concentration was relatively small, no definite conclusions can be drawn from this trend. Further experimentation remains to be done.

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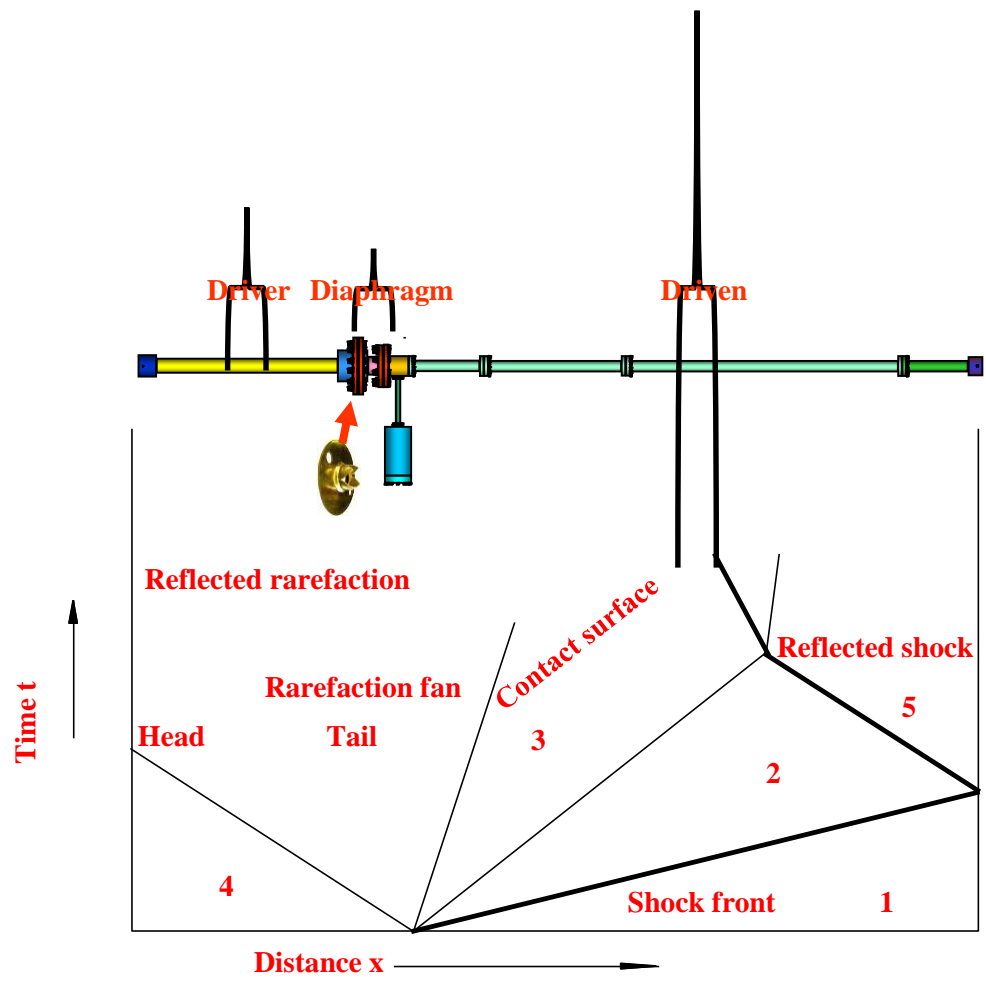


Figure 1

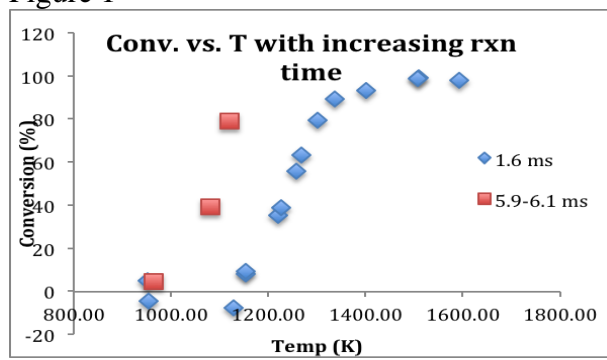


Figure 2

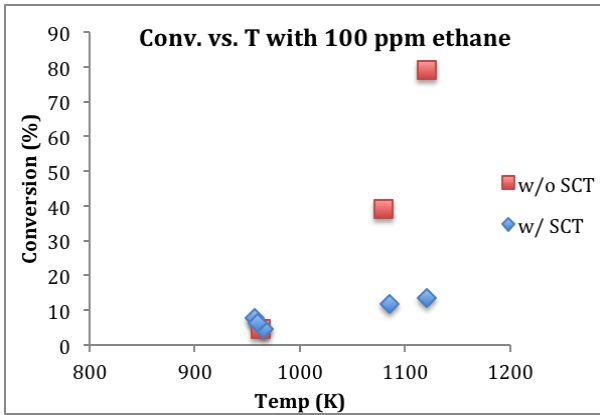


Figure 3

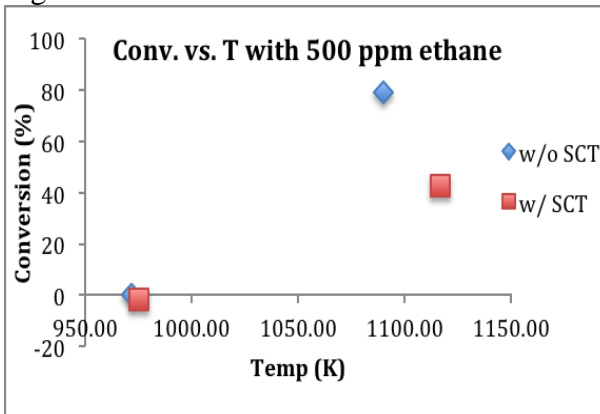


Figure 4

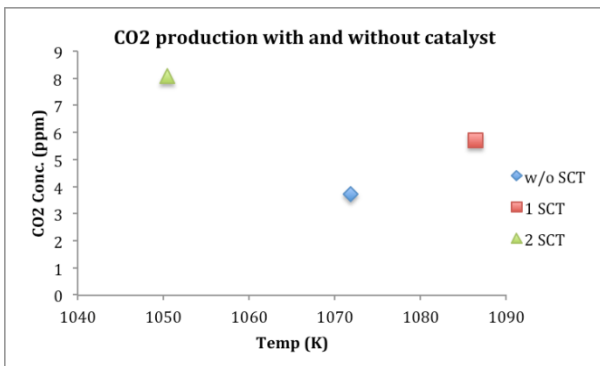
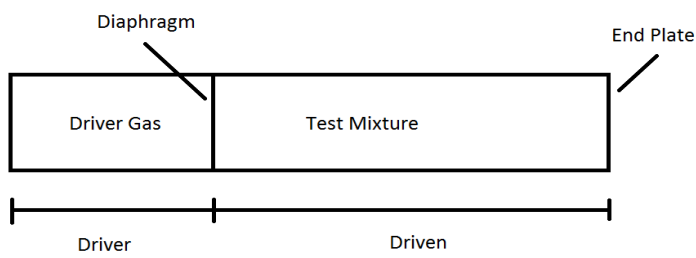


Figure 6



FIGURE