THE INFLUENCE OF INFRARED RADIATION ON ACETYLENE CONVERSION

by

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Where natural gas exists in large quantities, it is possible to consider its use as something other than a gaseous fuel. The production of liquid fuels, such as gasoline, is one possibility. For example, there is renewed interest in the pyrolysis of methane to acetylene which stems from the fact that acetylene proved to be a good feedstock for a number of specialty chemicals before its displacement by ethylene as the primary petrochemical building block[1,2]. In spite of a number of patents and news-briefs[3,4,5], a commercial route for converting acetylene to high-octane aromatics does not exist. In order to investigate this process, acetylene conversion studies were performed in our laboratory. Initially, both steady state and transient experiments were contemplated. An infrared radiation furnace was considered to be ideal for transient experiments because it had the capability of increasing the reaction temperature several hundred degrees within a few seconds. The purpose of this

communication is to compare experimental results obtained using the infrared furnace with those obtained using a resistance furnace. Results indicate that the use of infrared heating may be inappropriate for studying the effects of temperature on reaction rate for some reactions.

The experimental system involved a fixed-bed tubular reactor constructed from a transparent quartz tube having a length of 60 cm and an inner diameter of 1 cm. Both thermal and catalytic experiments were performed.

For the thermal experiments the tube was filled with broken opaque quartz particles (0.5-1mm). For the catalytic experiments, 5 g of catalyst was loaded into the centre of the reaction tube and the remainder packed with quartz particles. The reaction gas, composed of 10% acetylene and 90% nitrogen, was introduced into the reactor at a volumetric space velocity of 1500 h^{-1}. The reactor was operated at atmospheric pressure. The condensable reaction products were collected and analyzed by GC/MS (Varian 6000 and Finnigan ITD 700). The uncondensed products were analyzed on a Carle model AGC 111 S gas chromatograph equipped with thermal conductivity detectors.

Heat was provided to the reactor by means of two alternate systems. The first was an infrared gold image furnace (RHL-E410) obtained from ULVAC SINKU-RIKO which contained four infrared bar lamps as heating elements. This furnace offered a rapid heating capability, for example, 100°C/s compared with 20-35°C/min for most resistance furnaces. The

temperature controlling thermocouple was located inside the thermowell which ran axially along the reactor centreline. A second thermocouple in the well was used to monitor the axial temperature distribution. The second heating system was a three-zone electrically-heated furnace designed with resistance wire elements. Each of the furnace zones was controlled separately. Thermocouples in contact with the furnace tube provided temperature measurements for control. A series of thermocouples located at regular intervals in the thermowell permitted axial temperature measurements inside the reactor. With this system, furnace tube temperatures were adjusted to attain the required internal reactor temperature profile.

Figure 1 shows experimental data for acetylene conversion as a function of the reactor temperature, for both non-catalytic and catalytic experiments. The catalytic experiments were performed with a fluorinated alumina (Catapal SB) catalyst having a F/Al ratio of 1/10. Axial temperature gradients of 5 to 10°C were measured in the catalyst bed for both heating systems. In each case greater conversions were obtained when the reaction occurred in the presence of infrared radiation.

The effect of the infrared radiation on the thermal reaction shown in Figure 1 can be explained in terms of two phenomena. First, gas-phase acetylene absorption of infrared radiation in the 2900-3400 cm^{-1} frequency range has been demonstrated by Sheppard and Simpson[6]. When the energy for the thermal reaction is supplied by the infrared rays, vibrational excitation of the acetylene molecule occurs which weakens the C-H bonds. Second, the thermal conversion of acetylene which occurs only

at temperatures exceeding 500°C is believed to proceed via a free-radical mechanism[7]. Presumably free radicals are generated from the energy supplied by infrared radiation and these free radicals are responsible for the conversions observed in the non-catalytic experiments performed in the infrared furnace in the 200-500°C temperature range.

The effect of the infrared radiation on the catalytic reaction shown in Figure 1 can also be explained in terms of two phenomena. As in the thermal experiments, the gas-phase acetylene absorption of infrared radiation contributes to the acetylene reactivity by weakening the C-H bonds. In addition to this, however, Yates and Lucchesi[8] have demonstrated that both strong and weak interactions occur when acetylene adsorbs on alumina. The strongly chemisorbed species from acetylene are held normal to the alumina surface (interaction through C-H bond), while the weakly chemisorbed acetylene molecules are held flat on the alumina surface (interaction through C ≡ C bond). A similar adsorption on the fluorinated-alumina catalyst surface may contribute to the high acetylene conversions. The greatest conversions were observed when infrared excitation of acetylene and adsorption of acetylene on the catalyst surface were combined.

A significant difference was also observed in the products obtained from the catalytic experiments when carried out in the presence/absence of infrared radiation. In the former case, the product spectrum included hydrogen, ethylene, ethane, methane and a large fraction of condensable hydrocarbons. In the latter case, the major product was in the

condensable hydrocarbons range with ethylene, ethane, methane and light olefins (C_4's) present only in traces.

These results indicate that an infrared furnace is unsuitable for studying the effect of temperature on reaction rates. Higher temperatures were obtained by increasing the power to the furnace, which increased both the temperature and the intensity of infrared radiation. Therefore any changes in conversion were caused, in part, by an increase in temperature and, in part, by an increase in intensity of radiation.

In summary, two conclusions may be drawn. First, infrared radiation increases the conversion of acetylene in both thermal and catalytic reactions. Second, infrared furnaces are not suitable for measuring the effect of temperature on reactions which are influenced by infrared radiation.

References

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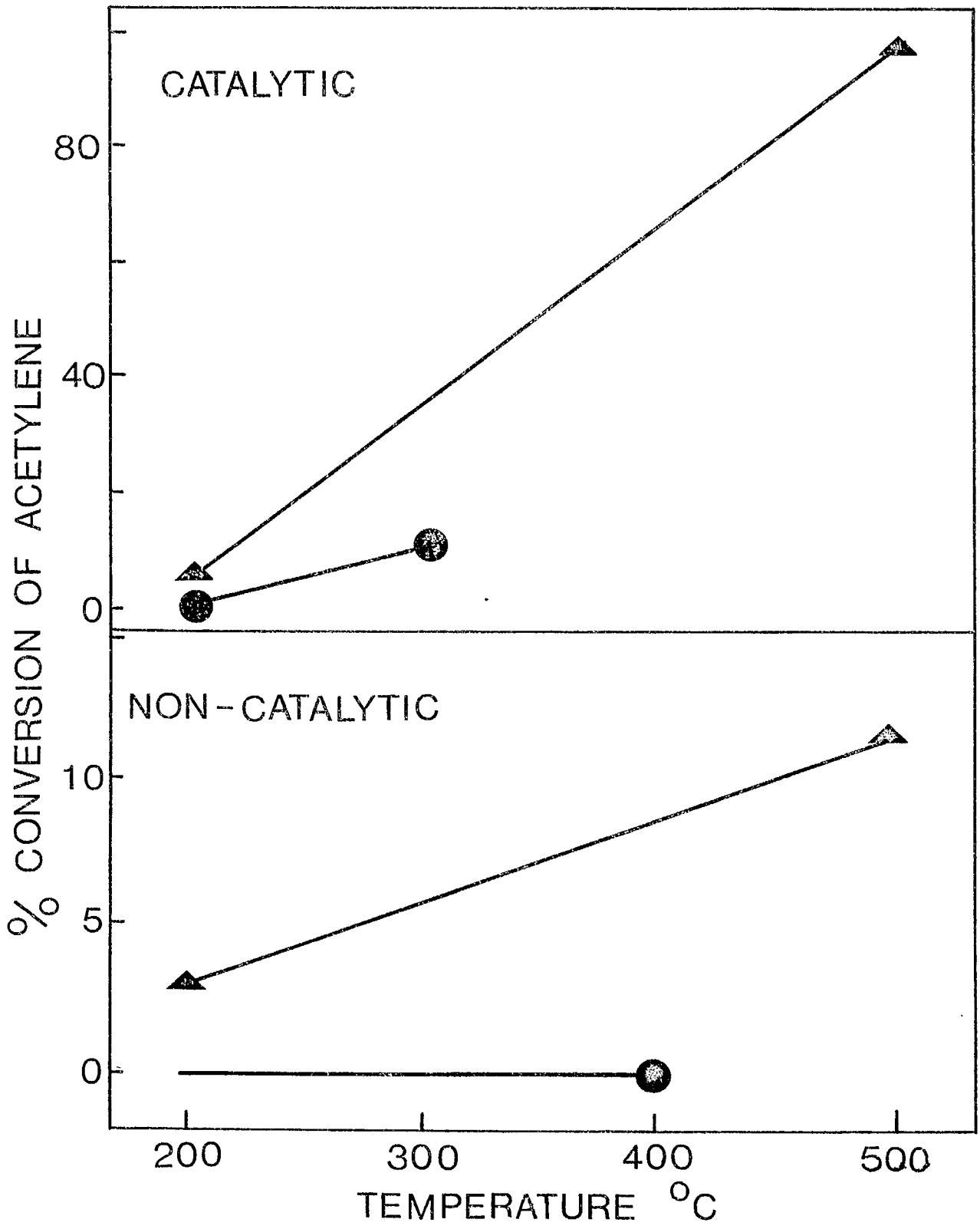
Figure 1 Per cent conversion of acetylene versus temperature

The upper graph contains catalytic data. The lower graph contains non-catalytic data. Triangles and circles represent data obtained using the infrared and electrical resistance furnaces, respectively.


CATALYTIC
80
40
0
NON-CATALYTIC
10
5
0
% CONVERSION OF ACETYLENE
200
300
400
500
TEMPERATURE °C