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Hydrogenation of Ethylene over Zinc Oxide
Effect of an Electrodynamic Field

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The effect of externally applied alternating electric fields on the hydrogenation of ethylene over randomly oriented zinc oxide surface has been studied. Reaction partial orders and activation energy were altered by the presence of an electric field. Variant behavior was observed, depending on the reaction temperature. At lower temperatures the effect of the field was to accelerate reaction rate and at higher temperatures, rate was decreased by the field.

I. INTRODUCTION

The ultimate goal in studying heterogeneous catalytic reactions is to provide information which will aid in the formulation of a general theory of catalysis which allows prediction of catalytic activity for any given reaction system. Such a theory is yet incomplete at best, though much has been learned in the past two decades in this regard. One discovery has been that electrical properties of semiconductor catalysts are often altered as activated processes take place on their surface. The availability of conduction electrons has thus been linked to the presence of electron seeking or donating molecules adsorbed on the semiconductor surface. Other related work has shown that the rates of such activated processes may be changed by introducing altervalent dopant substances into the lattice structure of the semiconductor or by irradiating the catalyst surface with light. More recently this same effect has been demonstrated by allowing the process to take place in the presence of an externally applied electric field (*1–11*). The latter technique allows more experimental flexibility since the chemical structure of the catalyst is not changed and the electronic structure may be rather easily varied. Relatively few chemical reactions have been studied under such conditions. These include the oxidation of CO and H_2 and the hydrogenation of benzene.

In this study the hydrogenation of ethylene over zinc oxide catalyst has been studied in the presence of an alternating electric field. Experimental conditions were of practical interest in that atmospheric pressure and bulk-randomly oriented catalyst surface were used. The hydrogenation of ethylene was chosen as the system since it is the simplest of the group of olefin hydrogenation reactions, and has been previously studied over zinc oxide without the presence of an electric field.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The reactor used in this study is illustrated in Fig. 1. The reactor enclosure consisted of a main body and two end covers of mild steel. Gas inlet and outlet ports, as well as electrical connections, were in the end covers. The main reactor body contained a catalyst chamber 0.75 in. long and 1.75 in. in diameter. Electrodes were placed on both ends of this chamber. Each electrode was insulated from the catalyst by an alundum fritted disc. The electrodes were perforated to allow passage of gases.

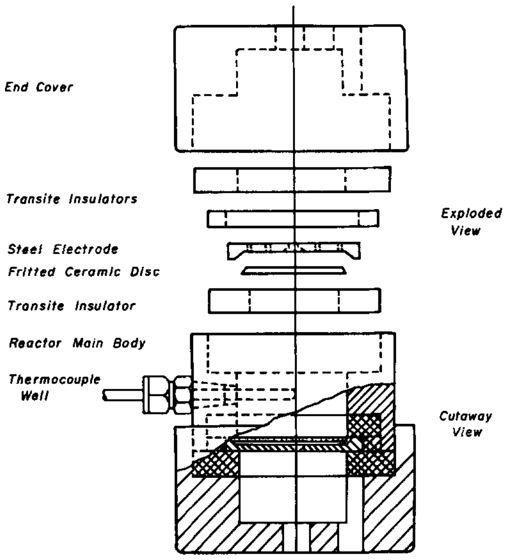

FIG. 1. Schematic of the experimental reactor.

A thermocouple was inserted through the wall of the main body into the catalyst chamber. The complete apparatus schematic is shown in Fig. 2. Further details are given elsewhere (*12*).

Reactants, ethylene (CP, 99.5% pure) and hydrogen (reactor grade, 99.998% pure) were passed through Englehard Deoxo purifiers and individually metered through Hastings-Radist thermal conductivity mass flow meters. Helium (reactor grade, 99.998% pure) was metered as a diluent through a Brooks rotameter. Metered gases were collected in a manifold, sent through a calcium chloride dryer, and preheated in a sand bath prior to introduction into the reactor. The reactor was wrapped in an electrically heated thermal blanket in order to obtain the desired reaction temperature. A reactor bypass allowed direct sampling of the reactor feed stream.

Gas analysis was by gas chromatography, using a Perkin-Elmer 154D model with thermal conductivity detector and 5 cc sample loop. A 10 ft section of 0.1875 in. copper tubing packed with 80–100 mesh Porapak Q served as the separation column and was operated at 50°C with a helium carrier gas rate of 40 cc/min.

The alternating electric field was produced by imposing a 60 cycle ac voltage across the two electrodes on either end of the catalyst chamber. No attempt was made to study the effect of varying the frequency because the power supply used did not have this capability.

The zinc oxide catalyst used was Harshaw Zn-0401E, 0.1875 in. extrudate with a surface area of 3 m^2/g and a pore volume of 0.26 cc/g (manufacturer specifications). The catalyst was crushed and screened either to 20–28 mesh or 35–48 mesh and then was activated. Activation of the zinc oxide was accomplished by heating in vacuum at 450°C for 1 hr followed by insertion into the reactor and reheating, in vacuum, at 300°C for 2 hr. Finally hydrogen was passed over the catalyst at 300°C for 0.5 hr followed by another vacuum treatment for 1 hr.

Reaction rate dependence on hydrogen partial pressure was determined by measuring reaction rates for various hydrogen flow rates, maintaining the ethylene flow constant and adjusting the helium flow to

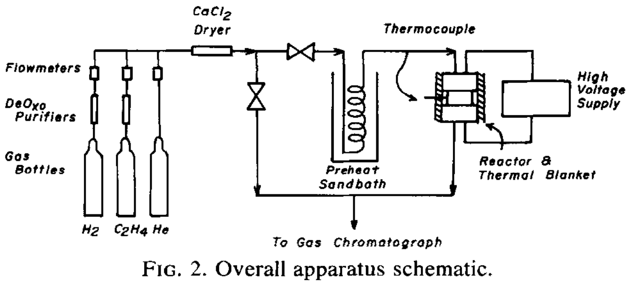

FIG. 2. Overall apparatus schematic.

obtain a constant total flow rate. An analogous procedure was followed to obtain the reaction rate dependence on ethylene partial pressure, in this case varying ethylene flow rate while maintaining hydrogen and total flow rates constant. The reaction rate was determined using the mass balance for a differential reactor, $-r = F_0X/m$, where r is the rate of reaction of ethylene, F_0 is the molar flow rate of ethylene, X is the ethylene fractional conversion, as determined by gas chromatography, and m is the mass of catalyst present.

Runs as just described were made both with and without the electric field and at several temperatures, allowing the determination of the electric field effect on reaction activation energy and partial orders.

III. RESULTS

The experimental observations can be best summarized as to whether or not the reaction was conducted in the presence of a field.

In the absence of a field, two distinct regions of interest were noted. At a temperature of 195°C, reaction orders of 0.39 and 0.77 were observed for hydrogen and ethylene, respectively. Below 150°C, the rate was approximately first order in hydrogen and zero order in ethylene, though scatter in the ethylene data below 150°C makes the latter observation questionable. Bozon-Verduraz and Teichner (*13*) report partial order of 0.3 and 0.7 for hydrogen and ethylene, respectively, at 162°C. At 210°C, they found values of zero for hydrogen and unity for ethylene. Dent and Kokes (*14,15*) reported the reaction to be one-half order with respect to hydrogen at room temperature. Figure 3 presents this information in graphical form for ethylene, and Fig. 4 for hydrogen. Definite trends are observed from the data presented from three independent sources. These trends indicate a change in the dominant mechanism as the reaction temperature is changed. Different behavior was observed by conducting the reaction in the presence of an electric field.

In the presence of the 60 Hz electric field of about 1,270 V/cm the ethylene order was zero at 86.5°C but was increased significantly above the zero field mean value of 0.14, to 0.5 at a temperature of 146°C in a 60 Hz field of about 1,150 V/cm. The hydrogen order at 86.5°C and 1,270 V/cm was reduced from an interpolated zero field value of about 0.9, to zero in the presence of a field and at 146°C and 1,150 V/cm was reduced from a zero field mean value of 1.3, to 0.65 in the pres-

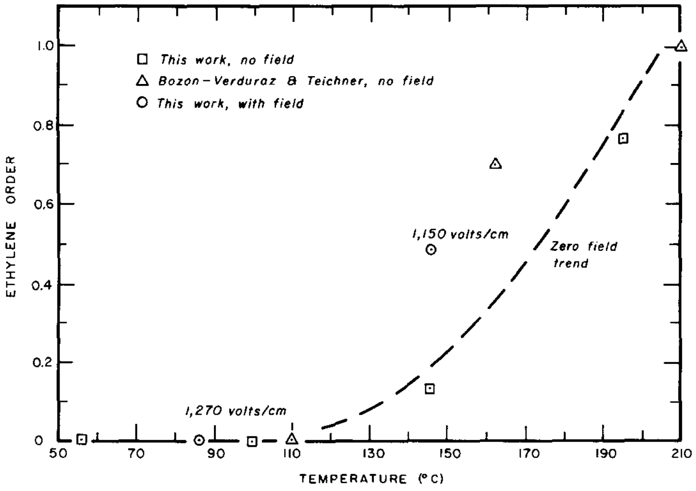

FIG. 3. Ethylene order–temperature dependence.

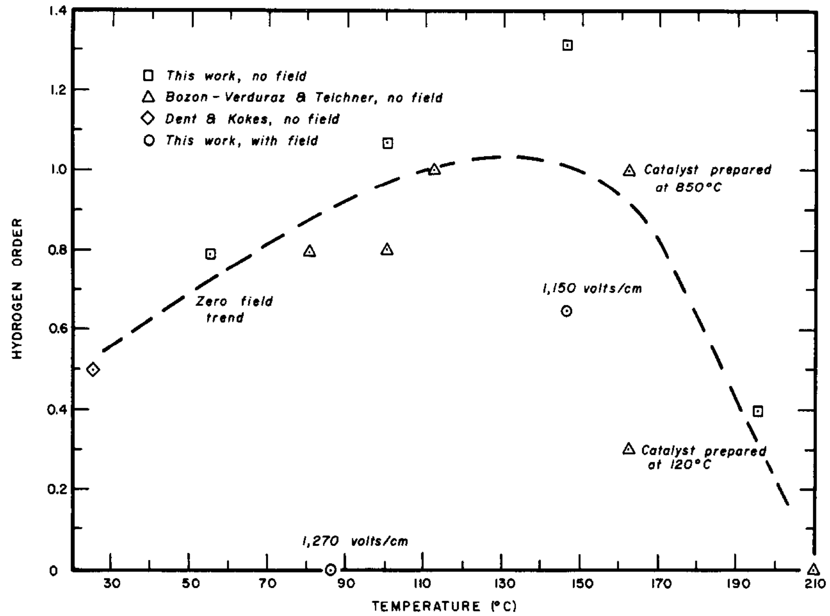

FIG. 4. Hydrogen order–temperature dependence.

ence of a field. These points are included on Fig. 3 and 4.

An Arrhenius plot for normalized rate data obtained at the various reaction temperatures without an electric field is shown in Fig. 5. The sudden change in the slope of this curve is indicative of a change in reaction mechanism. This change occurs within a temperature range of 137–149°C which is consistent with the observation in

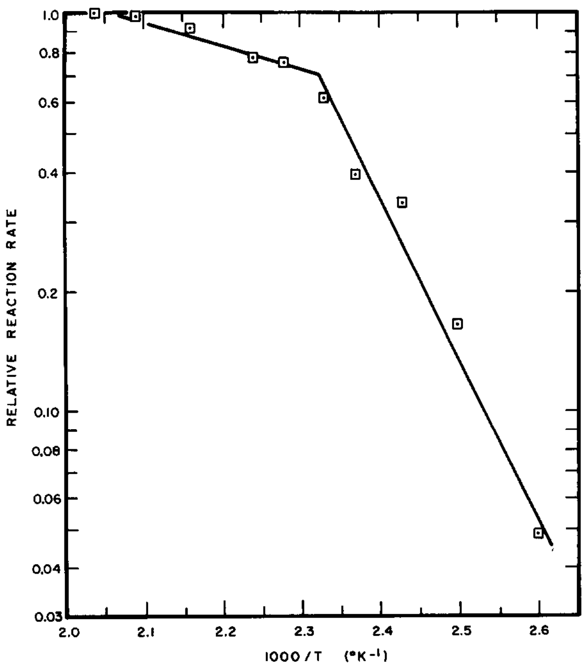

FIG. 5. Zero field Arrhenius plot.

this study that reaction order changed in the temperature range of 146–195°C. Bozon-Verduraz and Teichner (*13*) found that this transition occurred at temperatures ranging from 120 to 200°C depending upon the catalyst activation procedure used. Activation energies of 15.7 and 2.2 kcal/g mole, respectively, correspond to temperatures below and above the transition point. We observed these values to vary somewhat, depending on the method of catalyst activation. Bozon-Verduraz and Teichner (*13*) report corresponding values of 21 and 4.5 kcal/g mole.

Figure 6 illustrates the effect of the electric field on the activation energy. This data was taken by alternately turning a 60 Hz-1,270 V/cm field off and on for successive data points. This gives a very clear indication that the activation energy is dependent upon the presence or absence of the field. It is interesting to note that the lines intersect at a temperature of about 86°C. Above this temperature the reaction rate was reduced by the field. This phenomenon cannnot be explained by inductive heating caused by the presence of the field. If inductive heating were significant, the Arrhenius plots would not intersect, as inductive heating could not cause the decrease in reaction rate that occurred in the presence of the field at temperatures above 86°C. Since this series of runs was conducted below the temperature transition point, no break in either of the lines was noted. Activation energies are 11.5 kcal/g mole in the presence of the field and 17.0 kcal/g mole without the field. The difference in this zero field activation energy and the value of 15.7 kcal/g mole from Fig. 5 is attributed to method of catalyst activation and possibly a relaxation phenomenon observed when the field is turned on and off. The presence of minute quantities of acetylene at higher field strengths indicates that dehydrogenation processes are operating in parallel to the predominant hydrogenation reaction.

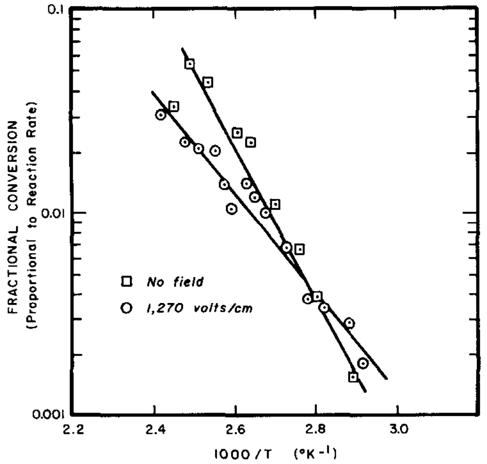

FIG. 6. Arrhenius plot with and without a field.

IV. DISCUSSION

Preparation of the zinc oxide catalyst for use proved to be a difficult problem. Several attempts at activating the catalyst for hydrogenation failed, presumably due to the exposure to air at some point in the activation procedure. Exposure to air results in the chemisorption of oxygen on the catalyst and its subsequent reaction with hydrogen to produce water which then poisons the catalyst. Heating the catalyst inside the reactor at 300°C in a vacuum followed by passing hydrogen over the catalyst finally resulted in observable hydrogenation activity. However, even with this procedure the catalyst activity varied from day to day making comparison of results taken on different days difficult. This was controlled to some extent during the latter stages of the study by passing helium over the catalyst overnight. During one test for reproducibility, hydrogen, ethylene, and helium flows were maintained constant at 68.0, 10.9 and 93.0 cc/min, respectively, at 146°C for 5 hr. During this time eight measurements of fractional conversion were made. The average value was 0.104 with a high of 0.108 and a low of

0.100. No trend was noticed suggesting the variance to be due to random errors. Following this run helium was passed over the catalyst bed overnight and a 6 hr run was made on the following day under the same conditions. The 10 measurements of fractional conversion made during this series had an average of 0.092 with a high of 0.112 and a low of 0.082. To insure that no catalyst deactivation had occurred during a series of runs during a day, the initial run was repeated at the end. No significant decay in activity was observed.

The mechanism for catalytic dehydrogenation of ethylene is still an open question, despite high research activity in this area. In this work we have demonstrated that an externally applied electrodynamic field does influence the reaction rate by altering the mechanism in some manner, as yet unknown. The use of such external stimuli would appear to have promise for the elucidation of the underlying mechanism.

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