

Dual Function Catalysis with the Metal at a Higher Temperature than the Support

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Maintaining the metal and nonmetal sites of a dual function catalyst at different temperatures is termed differential heating. A way has been found to maintain a temperature difference between the catalytic sites of the iron portion and the sites of the silica-alumina portion of a dual function catalyst. A radiofrequency induction heater was used to keep the iron at a higher temperature than the silica-alumina. The iron particles supported upon the silica-alumina were heated directly by the induction unit, while the silica-alumina was heated only by conduction of heat away from the iron particles. The iron temperature was determined using the temperature dependence of the hydrogenation of propylene over the iron. The silica-alumina temperature was determined: (a) by using the temperature dependence of the isomerization of cyclopropane over the silica-alumina and (b) by the adsorption of hydrocarbon upon the catalyst. Under one set of conditions a temperature difference of 58°C between the iron and the silica-alumina was indicated by the two reactions. The adsorption measurements had an even lower temperature for the silica-alumina. Among the important factors effecting an increase in temperature difference are: (a) increasing average catalyst temperature, (b) increasing ratio of carrier gas flow rate to catalyst weight, and (c) increasing the particle size and separating the two functional portions of the catalyst.

INTRODUCTION

This paper presents results showing that it is possible to maintain the two functions of an iron silica-alumina dual function catalyst at different temperatures by using a radiofrequency induction unit to heat the iron portion of the catalyst to a higher temperature than the silica-alumina. Maintaining the functions of the dual function catalyst at different temperatures is termed differential heating. Differential heating has been applied to dual function catalysts to alter their selectivity (1).

Radiofrequency induction heating occurs when electrical conducting materials are placed in an electromagnetic field produced by the alternating current passing through an induction coil. Differences in electrical potential are set up by the alternating magnetic field passing through the material to be heated, causing small circulating currents, called eddy currents,

within the material. These eddy currents produce heating.

With ferromagnetic materials, such as iron, there are two types of heating effects—the eddy current heating described above and hysteresis heating. Hysteresis heating results from the magnetic domains of the heated material trying to remain aligned with the magnetic field of the alternating current. Hysteresis heat is generated as long as the temperature remains below the Curie point of the sample. Above the Curie point, ferromagnetism is lost and hysteresis heating stops. The Curie point of iron is 770°C.

The ability of an induction heater to heat a metal particle decreases with decreasing size of the metal particle. Ferromagnetic materials can be inductively heated when dispersed as fine particles on supports, while nonferromagnetic metals cannot. Finely dispersed iron can be heated with

a radiofrequency induction unit at a frequency of 4 MHz. Silica-alumina is not heated at this frequency. By combining these two substances, a dual function catalyst is formed in which the iron is directly heated by the induction heater and the silica-alumina is heated only by conduction of heat from the iron. Experimental results are presented which show that under suitable conditions the iron can be maintained at a higher temperature than the silica-alumina. The iron temperature was determined using the temperature dependence of the hydrogenation of propylene over iron. The silica-alumina temperature was determined by two independent methods: (a) from the temperature dependence of the isomerization of cyclopropane over silica-alumina and (b) from the adsorption of hydrocarbons upon the catalyst.

EXPERIMENTAL METHODS

Apparatus

The apparatus is shown schematically in Fig. 1. Hydrogen carrier gas flowed through the reactor at atmospheric pressure with a flow rate of 40–180 ml/min. Reactant samples of 3 μ moles of either cyclopropane or propylene are injected into the hydrogen stream from the 1.76 ml

sample loop of the six port valve A (2) after the pressure had been measured with the pressure gauge. The 1.78 ml sample loop of the six port valve B (2) was used to bypass the reactor with gas samples for gas chromatography calibration. The entrance of the reactant into the reactor was noted by its passage through one side of the Gow-Mac hot wire detector, model 9285. The exit of the sample from the reactor was noted by its passage through the other side of the same detector. The reactor consisted of a U-tube of 4 mm i.d. Pyrex glass tubing. The catalyst occupied part of one side of the U-tube. The reactor was heated with an electrical resistance furnace during the calibrations. This furnace was replaced by a 5 kW, 4 MHz Lepel induction unit, Model T-5-3-Kc-A-B for the radiofrequency induction heating. The products were trapped in the loop at valve C (2) with liquid nitrogen. The trapped products were injected into the Perkin-Elmer Mark II, Model F-11 gas chromatograph for analyses by turning valve C and warming the trap.

Preliminary work suggested that the magnetic (hysteresis) effect is more important than the eddy current effect in the heating of the iron on the catalysts, since only the finely dispersed, supported materials which could be heated were ferromag-

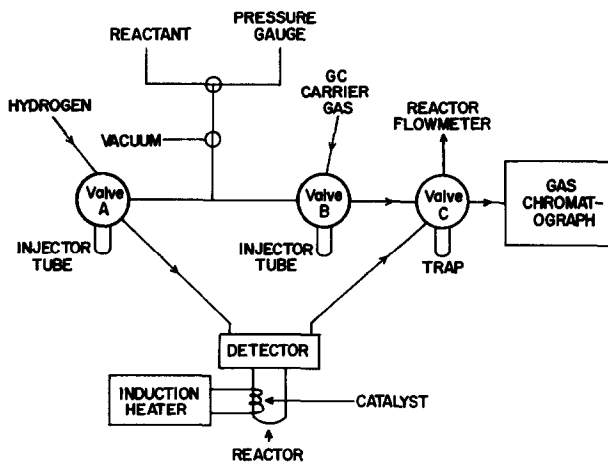


FIG. 1. Experimental apparatus.

netic. The induction heating was kept constant during the experiments at any one ratio of carrier gas flow rate to catalyst weight, but differed from one ratio to another.

The hydrogen used as carrier gas for the reactor system was passed through a Serfass Pd-diffusion purifier (Milton Roy Co.). The cyclopropane, propane, and propylene were CP grade from the Matheson Gas Products Co.

Catalyst Preparation

Iron on Silica. This catalyst was prepared by treating Davison 926 silica with an aqueous solution of ferric nitrate. The catalyst was dried overnight at 100°C and then heated in air for 2 hr at 260°C. The reduced catalyst contained 5% iron and had a BET surface area of 484 m²/g.

Silica-Alumina. This catalyst was a Davison silica-alumina cracking catalyst with a silica to alumina ratio of 6.7. The BET surface area was 402 m²/g.

Mixed Iron and Silica-Alumina. This catalyst was prepared by grinding together with a mortar and pestle Fe₃O₄ and some of the above silica-alumina. The mixture had an average Fe₃O₄ particle size diameter of 2×10^4 Å and an average silica-alumina particle size diameter of 50×10^4 Å as determined with an optical microscope. The mixture was pressed into disks, broken up, and the grains of 35/48 mesh size were selected. The catalyst had a BET surface area of 333 m²/g. The reduced catalyst had an iron content of 2.75 wt%.

Iron on Silica-Alumina. This catalyst was prepared by treating some of the Davison silica-alumina catalyst of 35/48 mesh size with an aqueous solution of ferric nitrate, drying overnight at 110°C, and heating in air for 2 hr at 260°C. The reduced catalysts contained 2.75 wt% iron having a BET surface area of 232 m²/g.

Particles of 35/48 mesh of each catalyst were reduced in the reactor with flowing

hydrogen at 450°C for 16 hr just prior to use. Each catalyst was brought to the desired reaction temperature while hydrogen was flowing over it.

Catalyst Temperature Measurements

The temperature difference between the iron and the silica-alumina of the iron silica-alumina catalyst was measured using two reactions and the hydrocarbon adsorption on the catalyst. The reaction of cyclopropane over the dual function catalyst gave an approximation of the temperature of the silica-alumina portion of the catalyst. It is shown below that under the experimental conditions the silica-alumina function catalyzes the decomposition of cyclopropane while iron does not to a significant extent. The curves in Figs. 2, 4, and 6 show the relation between temperature and the amount of cyclopropane decomposed for samples passing over catalysts heated uniformly with an electrical resistance furnace. An iron-constantan thermocouple taped to the outside of the Pyrex reactor tube at the middle of the catalyst bed length was used to measure the temperature. The temperature was held and measured to within $\pm 2.0^\circ\text{C}$. When the induction heating was used,

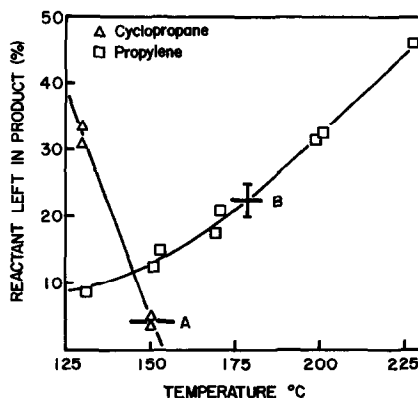


FIG. 2. Percentage of unreacted cyclopropane and propylene reactants versus temperature at a carrier gas flow of 511 ml/min/g of mixed iron and silica-alumina catalyst.

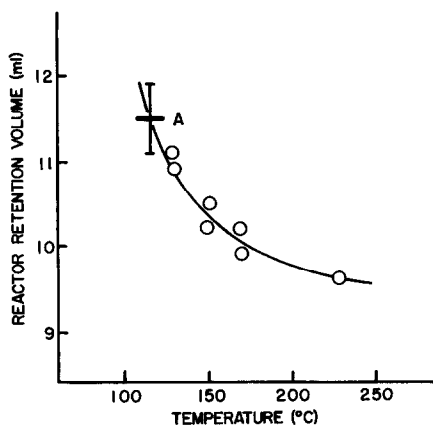


FIG. 3. Retention volume versus temperature at carrier gas flow of 511 ml/min/g of mixed iron and silica-alumina.

the amount of the cyclopropane reacting was used in conjunction with these calibration curves to indicate the average temperature of the catalytic sites on the silica-alumina.

The silica-alumina temperature was also measured by the adsorption of hydrocarbons upon it during the propylene hydrogenation reaction. The adsorption slows the passage of the hydrocarbons passing through the reactor. The adsorption affects the reactor retention volume, which is equal to the reactor retention time

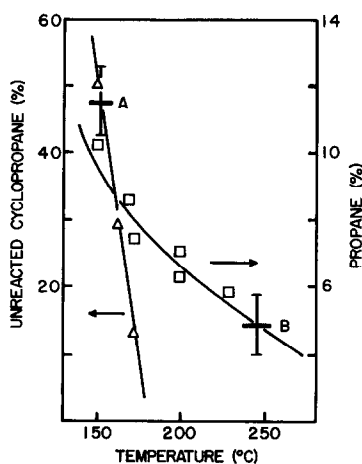


FIG. 4. Percentage of propane (□) from propylene reactant and unreacted cyclopropane (△) versus temperature at a carrier gas flow of 1360 ml/min/g of mixed iron and silica-alumina catalyst.

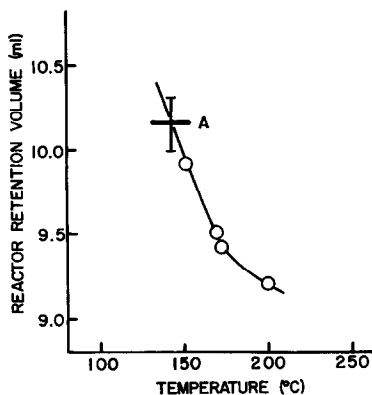


FIG. 5. Retention volume versus temperature at carrier gas flow of 1360 ml/min/g of mixed iron and silica-alumina catalyst.

multiplied by the carrier gas flow rate. The retention time is defined here as the time interval between the reactor detector responding to the sample going into the reactor and coming out of the reactor. The curves in Figs. 3 and 5 show the relation between retention volume and temperature for samples passing over catalysts heated uniformly with an electrical resistance furnace. The retention volume decreases with increasing silica-alumina temperature. When induction heating was used, the retention volume was used in conjunction with these calibration curves to indicate the average temperature of the adsorption sites on the silica-alumina.

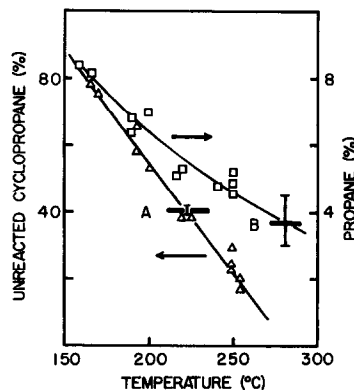


FIG. 6. Percentage of propane (□) from propylene reactant and unreacted cyclopropane (△) versus temperature at a carrier gas flow of 3750 ml/min/g of iron on silica-alumina catalyst.

The iron temperature was measured with the reaction of propylene and hydrogen to form propane. The reaction takes place over the iron and to a negligible extent over the silica-alumina (as shown below). The curves in Figs. 2, 4, and 6 show the relation between temperature and the amount of propane formed on propylene disappearing for samples of propylene reactant passing over catalysts heated uniformly with an electrical resistance furnace. When the induction heating was used, the amount of propylene reacting was used in conjunction with the calibration curves to indicate the average temperature of the catalytic sites on the iron.

RESULTS

Reactions over the Silica-Alumina Catalyst

Separate samples of the reactants cyclopropane and propylene were passed over 0.238 g of the silica-alumina catalyst in a hydrogen carrier gas stream flowing at 40 ml/min. The catalyst was heated with the electrical resistance furnace. The cyclopropane reacted readily to form propylene and was completely decomposed above 120°C. About 5% of the propylene was hydrogenated over the temperature range of 90–250°C.

Reactions over the Iron on Silica Catalyst

Separate samples of the reactants cyclopropane and propylene were passed over 0.266 g of the 5 wt% iron on silica catalyst in a hydrogen carrier gas stream flowing at 40 ml/min. Eight percent of the cyclopropane was hydrogenated to propane at 200°C. The amount hydrogenated decreased with decreasing temperature over the range of 200–120°C. The propylene was completely hydrogenated to propane over the 200–120°C temperature range.

The reactions over the silica-alumina

catalyst and the iron on silica catalyst indicate under the conditions used in this experiment silica-alumina catalyzes the isomerization of cyclopropane much more readily than it hydrogenates propylene, while iron is just the opposite. It catalyzes the hydrogenation of propylene much better than it isomerizes cyclopropane.

Reactions over the Mixed Iron and Silica-Alumina Catalyst

Differential heating was first shown to occur with the mixed iron and silica-alumina catalyst under two different conditions of flow rate to catalyst weight ratio.

Separate samples of the reactants cyclopropane and propylene were passed over 0.352 g of the 2.75 wt% iron and silica-alumina catalyst mixture in a hydrogen carrier gas stream flowing at 180 ml/min. This gave a carrier gas flow rate to catalyst weight ratio of 511 ml/min/g. The temperature results are given in Table 1. The calibration curve for cyclopropane and propylene reactions at this flow rate to catalyst ratio are shown in Fig. 2. Point A gives the percentage of cyclopropane ($4.1 \pm 0.7\%$)¹ in the product distribution when the induction heating was used in place of the furnace. This corresponds to an average temperature of the catalytic sites on the silica-alumina of $151 \pm 2^\circ\text{C}$.

Point B gives the percentage of propylene ($22.7 \pm 2.3\%$) in the product distribution with propylene as the reactant under the same conditions with the induction heater operating. The reactivity of the propylene indicates that the catalytic sites on the iron had an average temperature of $178 \pm 6^\circ\text{C}$.

The calibration curve of reactor retention volume versus temperature for the 511 ml/min/g conditions is shown in Fig. 3. Point A indicates a retention volume of 11.5 ± 0.4 ml for the propylene reaction

¹ Reproducibility is given throughout as 1 SD based on two to four repeat determinations.

TABLE 1
CATALYST TEMPERATURES

Catalyst:	Mixture of Fe and silica-alumina	Mixture of Fe and silica-alumina	Fe on silica-alumina
Flow/cat. wt (ml/min/g)	511	1360	3750
Fe Temp (°C), C ₃ H ₆ + H ₂	178	245	280
Silica-alumina temp (°C), cyclo-C ₃ H ₆	151	151	222
Silica-alumina temp (°C), adsorption	115	142	—
Differential temp (°C)	27	94	58

hydrocarbons when the induction heater was operating. This corresponds to an average temperature for the adsorption sites on the silica-alumina of $115 \pm 8^\circ\text{C}$.

The same catalyst was run again with increased induction heating using a smaller amount of catalyst to increase the ratio of carrier gas flow rate to catalyst weight. Separate samples of the reactants cyclopropane and propylene were passed over 0.044 g of the mixed iron and silica-alumina catalyst in a hydrogen carrier gas stream having a flow rate of 60 ml/min. This is a flow rate to catalyst ratio of 1360 ml/min/g. The temperature results are given in Table 1. The calibration curve for the cyclopropane reaction under these conditions is shown in Fig. 4. Point A gives the percentage of cyclopropane ($47.5 \pm 5.0\%$) in the product distribution when induction heating was used. This corresponds to an average temperature of $151 \pm 3^\circ\text{C}$ for the catalytic sites of the silica-alumina.

The calibration curve for the propylene reaction at a flow rate to catalyst ratio of 1360 ml/min/g is shown in Fig. 4 as the percentage of propane formed versus the temperature. Point B gives the percentage of propane ($4.9 \pm 0.9\%$) formed when the heating was changed to induction heating. The propylene reaction indicates that the catalytic sites on the iron had an average temperature of $245 \pm 23^\circ\text{C}$.

The reactor retention volume versus

temperature curve for the 1360 ml/min/g ratio is shown in Fig. 5. Point A indicates the retention volume of the propylene reaction hydrocarbons (10.15 ± 0.15 ml) when the induction heater was operating. These retention volume data indicate that the adsorption sites on the silica-alumina had an average temperature of $142 \pm 5^\circ\text{C}$.

Reactions over the Iron on Silica-Alumina Catalyst

Once the differential heating was shown to occur on the mixed iron and silica-alumina catalyst, a more intimate catalyst composition, namely, iron deposited on silica-alumina, was tested. Under suitable, more stringent conditions, including increased induction heating, the nonuniform heating was also demonstrated for this catalyst.

Separate samples of the reactants cyclopropane and propylene were passed over 0.048 g of the 2.75 w% iron on silica-alumina catalyst with a hydrogen carrier gas flow rate of 180 ml/min. This is a hydrogen carrier gas flow rate to catalyst weight ratio of 3750 ml/min/g. The temperature results are given in Table 1. The calibration curve for the cyclopropane reaction at 3750 ml/min/g is shown in Fig. 6. Point A gives the percentage of unreacted cyclopropane ($40.3 \pm 1.1\%$) when the induction heater was operating. Thus, the cyclopropane reaction indicates that the catalytic sites on the silica-

alumina portion of the catalyst had an average temperature of $222 \pm 2^\circ\text{C}$.

The calibration curve for the propylene reaction at 3750 ml/min/g is shown in Fig. 6. Point B gives the percentage of propane ($3.7 \pm 0.7\%$) formed during the induction heating. This corresponds to a temperature of $280 \pm 30^\circ\text{C}$ for the catalytic sites on the iron portion of the catalyst.

The flow rate and temperature were too high under these conditions for retention volume measurements, so the silica-alumina adsorption temperature could not be determined.

DISCUSSION

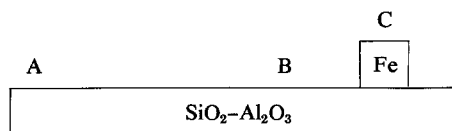
From the results of the cyclopropane and propylene reactions over the iron and silica catalyst, it is seen that the iron hydrogenates the propylene to propane in the presence of hydrogen, but does not affect the cyclopropane appreciably. The results of these reactions over the silica-alumina catalyst show that the silica-alumina catalyzes the isomerization of the cyclopropane but does not appreciably hydrogenate the propylene. Thus, the isomerization of cyclopropane can be used to indicate the temperature of the silica-alumina function of an iron silica-alumina catalyst, while the propylene hydrogenation can be used to measure the temperature of the iron portion.

Differential heating is shown to occur with both the mixed iron and silica-alumina catalyst and the iron supported on silica-alumina catalyst. At a flow rate to catalyst weight ratio of 511 ml/min/g, the mixed iron and silica-alumina catalyst had a temperature difference (defined as the difference between the iron temperature measured by propylene hydrogenation and the silica-alumina temperature measured by the cyclopropane reaction) of 27°C . At the flow rate to catalyst weight ratio of 1360 ml/min/g, the same catalyst had a temperature difference of 94°C . The increase in temperature difference is due to

two effects. Firstly, the temperature difference is increased as the average temperature of the catalyst is increased. Secondly, the temperature difference is increased as the ratio of the carrier gas flow rate to catalyst weight is increased. Both effects are due to increase in removal of heat from the catalyst by the gas passing through the reactor. The carrier gas removes heat from both the iron and the silica-alumina. The result is that in order to maintain the silica-alumina at the same temperature with increasing flow to catalyst weight ratio, i.e., increased heat loss, the iron must be maintained at an even higher temperature by increasing the induction heating. By taking advantage of these two effects, the experimental conditions could be chosen to produce differential heating on the iron supported on silica-alumina catalyst. This was done by using a small amount of catalyst, a high flow rate, and using the maximum power of the induction heater to produce as high a temperature as possible.

At the resulting flow rate to catalyst weight ratio of 3750 ml/min/g, a temperature difference of 58°C was produced on the iron supported on silica-alumina catalyst. This temperature difference is considerably lower than the 94°C temperature difference of the mixed iron and silica-alumina catalyst. The iron and silica-alumina are much more intimately bound in the iron on silica-alumina catalyst than in the mixed iron and silica-alumina catalyst. This suggests another factor which may affect differential heating: The temperature difference is increased as the areas of the particles of the two catalyst functions (iron and silica-alumina) are increased and separated.

A diagram depicting a small segment of the catalyst is as follows:



The silica-alumina is coolest at site A because it is the farthest from the iron particle. Here is where the hydrocarbon adsorption predominantly takes place. The retention volume, therefore, reflects the average temperature of the cooler parts of the catalyst. The silica-alumina is hottest at site B, because of its close proximity to the iron particle. It is in these hotter areas of the silica-alumina portion of the catalyst that the cyclopropane isomerization takes place. Thus, the cyclopropane reaction reflects a higher average temperature than the retention volume.

The catalytic site C on the iron is hotter than either A or B. Under suitable experi-

mental conditions, such as those given above, the two kinds of catalytic sites on a dual function catalyst can be maintained at significantly different temperatures.

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