Performance of Periodic Pulse Technique (Part 1)

Dehydrogenation of Cyclohexane on a Platinum-Alumina Catalyst

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The periodic pulse technique was applied to the dehydrogenation of cyclohexane on a platinum-alumina catalyst to characterize the periodic pulse technique. Both the pulse width and the period, parameters to characterize the periodic feed of pulses, had significant effects on the conversion of cyclohexane. Small pulse widths and large periods were favorable for large conversion. When the time average pressure was constant, the optimum values of pulse width and period for the largest conversion were found to exist. Under such conditions, the conversion was higher than that in the flow technique, and even higher than the equilibrium conversion based on time average pressure.

1. Introduction

The pulse reaction technique is characterized by pulsed feed of one or of all reactants. It causes some peculiar phenomena such as chromatographic separation in the catalyst bed and the extensive tailing of chromatographic peak of products¹⁾. Such characteristics make it possible to measure the kinetic parameters which cannot be easily measured with the conventional flow technique^{2)~5)}. The present authors proposed another possible application, that is, industrial applications of the pulse technique^{6),7)}, because it can result in conversion or in selectivity which is markedly higher than by the conventional flow technique in certain types of reactions⁷⁾. In the sort of reaction, $A \rightleftharpoons R + S$, the conversion can be higher than the equilibrium conversion, because the reverse reaction is minimized by the separation between reaction products R and S. The present authors have reported on conversion higher than the equilibrium in the dealkylation of cumene on a silica-alumina catalyst⁸⁾ and 100% conversion on a HY zeolite catalyst⁹⁾.

The periodic feed of pulse is necessary for industrial applications, but only a few papers have been published on the subject. Gore¹⁰⁾, Chieh and Tsang¹¹⁾, and Schweich and Villermaux¹²⁾ investigated the periodic pulse technique on a simplified model by computer simulation and discussed the need for more suitable factors to attain

better conversion. Matsen et al.¹³⁾ dosed cyclohexane pulses repeatedly with a microsyringe in the dehydrogenation of cyclohexane, and obtained under the optimum conditions 30% greater conversion than the equilibrium value. In their experiment, however, the pulse feed shape was not well defined, because cyclohexane pulse was dosed with a microsyringe. Furthermore, such a shape of pulse dosed with a microsyringe-dose not seem industrially practical. The present authors developed a periodic pulse technique with rectangular pulse¹⁴⁾ and applied it to the characterization of oxide catalysts in the oxidation of olefins^{15,16)}.

The present series is a systematic experimental investigation to clarify characteristics of the periodic pulse technique. In the present paper, the periodic pulse technique was applied to the dehydrogenation of cyclohexane on a platinum-on-alumina catalyst. Since this reaction is one of the most frequently investigated reactions with the pulse technique, it should be most suitable for characterizing the technique. The application of the technique to more practical reactions, such as dehydrogenation of ethylbenzene and oxidative dehydrogenation of isobutyraldehyde and others, will be reported in subsequent papers.

2. Experimental

2.1 Periodic Feed of Pulse

In the continuous flow technique, a mixture of reactant and carrier gas is fed continuously with a constant partial pressure of reactant. Therefore, the feed can be characterized by two parameters: the total feed rate and the partial pressure of the reactant. In the periodic pulse technique with

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A : Carrier gas flows continuously
 B : Carrier gas and reactant flow alternately
 t₀ : Pulse width, t_p : Period, F_r and F_g : Feed rate of reactant and carrier gas, respectively,
 F_r : Average feed rate of reactant

Fig. 1 Diagram of Periodic Feed of Pulse

rectangular pulse, the feed is characterized by pulse width, t₀, and period, t_p, as well as total feed rate and partial pressure. The time average pressure is more significant than the partial pressure in the reactant pulse, when a comparison is made with the flow technique. The comparison should be made on the basis of the total amount of feed. The time average pressure can be calculated from the above-mentioned parameters as shown below. There can be two different ways to feed the pulse periodically as shown in **Fig. 1**. In case A, the carrier gas flows continuously with a constant flow rate, while the reactant is fed periodically only for a short time, termed the pulse width. The partial pressure of reactant in the pulse, which hereinafter will be called the pulse pressure, P_r, is calculated from the following equation.

$$P_r = P_{\text{total}} \times \frac{F_r}{F_t + F_g} \quad (1)$$

where P_{total} is the total pressure, and F_r and F_g are the feed rates of reactant and carrier gas, respectively. The time average pressure, P_r, is calculated from the feed rate of carrier gas, F_g, and the average feed rate of reactant, F_r = F_r (t₀/t_p), or from the total amount of carrier gas, F_g · t_p, and reactant, F_r · t_p, fed for a given period.

$$\bar{P}_r = P_{\text{total}} \times \frac{\bar{F}_r}{\bar{F}_r + F_g} = P_{\text{total}} \times \frac{F_r \cdot t_0}{F_r \cdot t_0 + F_g \cdot t_p} \quad (2)$$

In case B, the carrier gas and the reactant are fed alternately. The pulse pressure is identical

with the total pressure, and the time average pressure can be calculated from the following equation.

$$\bar{P}_r = P_{\text{total}} \times \frac{F_r \cdot t_0}{F_r \cdot t_0 + F_g \cdot (t_p - t_0)} \quad (3)$$

The equilibrium conversion, X_e, was calculated from the following equation.

$$K_p = (P_{\text{total}})^3 \frac{27X_e^4}{(1-X_e) \cdot [(P_{\text{total}}/P) + 3X_e]^3} \quad (4)$$

This equation indicates that the equilibrium conversion depends on the partial pressure of cyclohexane. Thus, the time average pressure should be used as the partial pressure in the periodic pulse technique when a comparison is made between periodic pulse technique and flow technique. An equilibrium constant, K_p, was obtained from the data of Rossini¹⁷.

2.2 Experimental Procedure

Fig. 2 shows a diagram of experimental apparatus, which is similar to the conventional apparatus of flow technique except that a microfeeder was controlled with an electric circuit constructed with timers and relays so that the microfeeder could be driven only during the time corresponding to the pulse width. A motor with a brake was used to drive the microfeeder, because the response of an ordinary motor is inadequate to feed cyclohexane as rectangular pulse. The evaporator was similar to the conventional sample inlet of gas chromatography. The temperature of evaporator had a large effect on the shape of the pulse, and so it was carefully decided in preliminary experiments by measuring the shape of the pulse with a thermal conductivity detector connected directly to the evaporator. A three way solenoid valve

1. 3-way solenoid valve, 2. Pressure regulator
 3. Evaporator, 4. Microfeeder, 5. Timer circuit
 6. Reactor, 7. Furnace, 8. Catalyst, 9. Temperature controller, 10. mV meter, 11. Dry ice-cooled trap, 12. Soap film meter

Fig. 2 Schematic Diagram of Apparatus for Periodic Pulse Technique

was installed to feed nitrogen, as carrier gas, alternately with cyclohexane, but it was not used in the present study. Nitrogen flowed continuously with a constant flow rate, or, in other words, only case A in **Fig. 1** was examined in the present study.

The reactor was a stainless steel tubing with an inside diameter of 8 mm, at the center of which a stainless steel tubing with an outside diameter of 3 mm was installed as a thermocouple sheath. The reactor was heated with an electrically heated furnace. The temperature was monitored with a thermocouple at the center of the reactor. The temperature was essentially constant, though the pulse of cyclohexane was fed periodically. The reaction product was collected in a trap cooled with a dry ice-acetone bath, and analysed with a gas chromatography with a $2\text{ m} \times 4\text{ mm}$ column of DOP on Celite 545 at 70°C .

A guaranteed reagent of cyclohexane was used without further purification. Nitrogen was dried by passing through a column of silica gel. The catalyst was a platinum catalyst supported on activated alumina. It was prepared by imregnating Sumitomo Activated Alumina (KAT-6, 28~35 mesh) with H_2PtCl_6 aq. solution to give 0.6 wt% of platinum. The catalyst was calcined at 550°C for 1 hr and reduced in a flow of hydrogen at 450°C for 3 hr. Standard reaction conditions were as follows; catalyst weight was 4.5 g, reaction temperature was 200°C , feed rate of nitrogen was 0.0536 mol/hr (20 ml/min), and feed rate of cyclohexane in periodic pulse experiments was 0.181 mol/hr.

3. Results and Discussion

3.1 Separation between Reaction Products

The dehydrogenation of cyclohexane was examined with the pulse technique by several groups^{12),13),18)}, and it was confirmed that hydrogen was separated from benzene in the catalyst bed. The reactor in the present study was significantly different from those used in the references^{12),13),18)}. The latter were similar to the gas chromatographic column rather than the conventional flow reactor. So the separation between hydrogen and benzene in the present reactor was confirmed under the reaction conditions. **Fig. 3** shows a chromatogram obtained with a thermal conductivity detector connected directly with the reactor. Helium was used as a carrier gas. A chromatographic peak of cyclohexane was not obvious, though the conversion was about 50%. This result indicated that

Pulse width : 5.5 sec, H_2 flow rate : 20 ml/min

Fig. 3 Chromatogram of Effluents

cyclohexane was not appreciably separated from benzene. On the other hand, hydrogen was clearly separated from benzene. This result suggests that the conversion can be higher than the equilibrium conversion, because the reverse reaction, i.e., hydrogenation of benzene, is minimized by the separation of hydrogen pulse from the benzene pulse.

3.2 Effect of Pulse Width

Fig. 4 shows the effect of pulse width on the conversion at a constant period and feed rate of cyclohexane. It was theoretically shown that the conversion depended significantly on the pulse width in the reaction of the sort $A=R+S^{1)}$. The conversion at sufficiently large pulse width was identical to the flow technique where the partial pressure of reactant was equal to the pulse pressure, and it increased with decreasing pulse width. And at sufficiently small pulse width, the conversion

Broken lines : Equilibrium conversion for N_2 flow rate of 20 ml/min (upper line) and 10 ml/min (lower line).

Fig. 4 Effect of Pulse Width at Constant Period

could be higher than the equilibrium conversion based on the pulse pressure. This tendency was confirmed in the dealkylation of cumene with the conventional single pulse technique⁸⁾. In **Fig. 4**, the period and the pulse pressure were kept constant and the carrier gas flowed continuously. Therefore, the situation was quite similar to the single pulse technique except for the repetitive feed of pulse. The results also was close to that of the single pulse technique. The conversion was significantly higher than the equilibrium value shown by the broken lines especially at small pulse widths. The conversion decreased with increasing pulse width, and was close to the equilibrium conversion at large pulse width.

3.3 Effect of Pulse Pressure

Fig. 5 shows the effect of pulse pressure on the conversion with constant period and with constant pulse width (closed circles) or with constant time average pressure (open circles). A sintered catalyst was used only in this run. Therefore the conversion in this run was lower than that in other runs. When the pulse width was constant, the conversion decreased with increasing pulse pressure. The reaction order may be fractional or nearly zero at the reaction temperature in the present study (200°C). The dehydrogenation of cyclohexane on the platinum catalyst is said to be zero or nearly zero order at 150°C¹⁹⁾, and first order at 300°C²⁰⁾. In the first order reaction, the conversion in the pulse technique is equal to that in the flow technique¹⁾. While, in the zero order reaction, the conversion should be inversely proportional to the partial pressure of the reactant in the flow technique, but in the pulse technique the zero order reaction, sometimes, behaves as a first order reaction or a fractional order reaction²¹⁾.

Fig. 5 Effect of Pulse Pressure

The relation between conversion and pulse pressure in **Fig. 5** is intermediate between first order reaction and zero order reaction, as is expected from a fractional or near zero order reaction.

When the time average pressure was constant, the conversion was maximum at intermediate pulse pressure, as shown by the empty circles in **Fig. 5**. The time average pressure can be determined by pulse pressure and pulse width, when the period and the flow rate of carrier gas are constant. To keep the time average pressure constant, a small pulse pressure should be accompanied with a long pulse width and vice versa. The results in **Fig. 5** suggest that at small pulse pressure the effect of pulse width predominates and at large pulse pressure the effect of pulse pressure predominates. Both large pulse pressure and pulse width resulted in small conversion, as mentioned above.

Fig. 6 Ratio of Conversion to Equilibrium Conversion (X/X_e) in Flow Technique (▼) and Periodic Pulse Technique (○, ●)

3.4 Effect of Flow Rate of Carrier Gas

The effect of carrier gas flow rate was a little puzzling. Curves 1 and 2 in **Fig. 4** were obtained with the same feed rate of cyclohexane and the same period but with a different flow rate of nitrogen. As can be seen from **Fig. 4**, low flow rates, which should correspond to large contact times, resulted in low conversions at the same pulse width. When the results at the same time average pressure are compared, the conversion is larger for low flow rates than for large flow rates, as shown in **Fig. 6** in which the abscissa is the time average pressure, and the ordinate is the ratio of the conversion to the equilibrium conver-

sion based on the time average pressure.

3.5 Effect of Period

In **Fig. 7**, the conversion was plotted against pulse width at various periods. The plot at a period larger than 180 sec gave one curve in which the conversion decreased with increasing pulse width. At a period smaller than 180 sec, the relation between conversion and pulse width was similar to that at the larger period mentioned above; but the conversion decreased with decreasing period. If the conversion is plotted against the period for various pulse widths, the conversion will increase with period below 180 sec and remain constant above it. When the period is sufficiently large, the conversion should be the same as that in the single pulse reaction and should be the maximum conversion. The conversion remains

Fig. 7 Effect of Period on the Relation between Conversion and Pulse Width

Broken lines : Equilibrium conversion for $\bar{P}_r = 0.090$ atm (upper line) and 0.175 atm (lower line)

Fig. 8 Effect of Period at Constant Time Average Pressure

constant, as the period decreases until the critical value where the hydrogen peak overlaps the benzene peak from the previous pulse. Below the critical value, hydrogen and benzene recombine to form cyclohexane which decreases the conversion level. The critical value in **Fig. 7** was 180 sec, which seemed to be smaller than the value expected from the chromatogram in **Fig. 3**. But there existed some bending and dead space, which would result in some tailing, between the catalyst bed and the thermal conductivity detector in the apparatus to measure the chromatogram. Taking this into account, the critical value in **Fig. 7** can be regarded as being in agreement with the chromatogram in **Fig. 3**.

Fig. 8 shows the relation of conversion with period at constant time average pressure. The pulse pressure was kept constant, but the pulse width was changed so that the ratio of pulse width to the period could be constant. The conversion had the maximum value near the 150 sec period. Periods smaller than that would result in the overlapping of hydrogen pulse with benzene pulse from the previous pulse, which decreases the conversion. Large periods should be accompanied with large pulse widths to keep the time average pressure constant, which also decreases the conversion.

As can be seen in **Fig. 8**, at the time average pressure of 0.090 atm, the conversion was larger than the equilibrium conversion based on the time average pressure.

3.6 Comparison with Flow Technique

Fig. 6 shows a comparison between the periodic pulse technique and the flow technique. It should be noted that the comparison was made on the basis of the time average pressure, that is, the comparison was made at the same amount of cyclohexane fed for a period, but not for a pulse width. Thus, the high conversion in **Fig. 6** corresponds to a high space time yield. At large time average pressure, the conversion in the periodic pulse technique did not exceed the conversion in the flow technique. On the other hand, at small time average pressure, the conversion in the periodic pulse technique was larger than the conversion in the flow technique, and it was even larger than the equilibrium conversion which cannot be exceeded in the flow technique. It follows that a higher space time yield than that expected from the equilibrium conversion can be expected by the periodic pulse technique.

3.7 Optimum Operation

The present authors showed that the conversion of the reaction of the sort $A=R+S$ was large when the pulse width was small and the separation factor was large, and that there would be the optimum period to obtain high conversion in the periodic pulse technique⁷⁾. A similar conclusion was obtained by several groups^{10)~12)}; an impulse-like feed and the control of pulse frequency were said to be favorable for obtaining high conversion. But no experimental examination has been done.

Only one kind of catalyst was used in the present study. Therefore, the effect of separation factor is not clear. The effect of pulse width shown in **Fig. 4** was in good agreement with the prediction and with the experimental result in the dealkylation of cumene⁸⁾; the conversion increased with decreasing the pulse width. But it should be noted that the results in **Fig. 4** were obtained under constant pulse pressure and period. The decrease in the pulse width is accompanied with a decrease in the time average pressure. When the time average pressure remained constant, smaller pulse widths did not always lead to an increase in the conversion. In **Fig. 8**, the pulse width was changed in proportion to the period so that the time average pressure could be constant. As is evident from **Fig. 8**, the conversion took the maximum value at some intermediate value of the period, that is, at some intermediate pulse width, but not at the smallest pulse width. In **Fig. 5**, the pulse width was changed inversely proportional to the pulse pressure. The conversion assumed the maximum value at the intermediate pulse width.

Prediction concerning the optimum period was supported by the results shown in **Fig. 8**. It is not clear at high time average pressures, but evident at low time average pressures, i.e., at small pulse width, that there is the optimum value of period which leads to a better conversion.

4. Conclusion

The feeding in the pulse reaction technique is characterized by the pulse width and the period as well as the feed rates of the reactant and carrier gas which are parameters of the feeding in the

flow technique. A markedly high conversion can be obtained, when the pulse width is sufficiently small and the period is larger than the critical value where the hydrogen peak overlaps the benzene peak from the previous pulse. When the time average pressure of reactant is constant, there are optimum values of both the pulse width and the period. The optimum value of the period was a little smaller than the critical value of the period mentioned above. These optimum values lead to a conversion higher than not only the conversion in the flow technique but also the equilibrium conversion based on the time average pressure.

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要 旨

周 期 的 パ ル ス 法 (第 1 報)

白金-アルミナ触媒上でのシクロヘキサン脱水素反応

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パルス反応法においては触媒層中における成分間のクロマトグラフ的な分類のために、選択率や転化率が非常に大きくなることがあり^{1),6),7)}, 工業反応装置としても興味深い¹⁾。このような観点から、原料パルスを周期的に供給する周期的パルス法の実験的検討がなされているが^{11)~14)}, いまだ十分とは言えない。本シリーズでは、各種反応に周期的パルス法を応用し、その特徴と応用性を明らかにすることを目的としたもので、本研究では、白金アルミナ触媒上でのシクロヘキサンの脱水素反応^{10),11),16)}を行った。

周期的パルス法では二通りのパルス供給法が考えられる(**Fig. 1**)。キャリアガスを連続的に流す場合(A)と反応物とキャリアガスを交互に流す場合(B)とである。実験装置(**Fig. 2**)および実験操作はシクロヘキサン供給用マイクロフィーダーをタイマー回路により断続的に駆動させた他は通常の流通反応と同様である。この反応装置に熱伝導度型検出器を直結し、生成物の H_2 とベンゼンがクロマトグラフ的に分離するこ

とを確認した(**Fig. 3**)。周期的パルス法における転化率はパルス圧(パルス供給中のシクロヘキサン分圧: P_r)を基準として計算した平衡転化率より著しく大きかった(**Fig. 4**)。また、流通法と比較するために、一定時間(1周期)内に供給された全シクロヘキサン量とキャリアガス量を基に計算した時間平均圧($\bar{P}_r$)を定義し、それを基に比較したところ、周期的パルス法の転化率は流通法の転化率や平衡転化率より大きかった(**Fig. 6**)。

周期的パルス法に特有なパラメーターはパルス幅(t_0)と周期(t_p)であるが、それらの影響は著しかった。周期およびパルス圧が一定の場合(**Figs. 4, 7**)、パルス幅が小さくなると転化率は非常に大きくなった。時間平均圧を一定とした場合(**Figs. 5, 8**)には、転化率を最大とするパルス幅の最適値があった。周期の影響も非常に大きかった(**Figs. 7, 8**)。

以上のように、周期を大きく、パルス幅を小さくすることにより転化率を著しく大きくすることができる。また、最適のパルス幅と周期を選ぶことにより、空時収量を流通法において平衡から期待される値以上にすることも可能である。

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Keywords

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