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AN EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN A POROUS CATALYST DUE TO PHASE TRANSITION

DONG HYUN KIM AND YOUNG GUL KIM
 Department of Chemical Engineering,
 Korea Advanced Institute of Science,
 P.O. Box 150, Chongyangni, Seoul, Korea

Up to four multiple steady states were experimentally observed by hydrogenating cyclohexene on a Pt/Al₂O₃ catalyst having bimodal distribution. The catalyst, in the form of 3/16-in. by 3/16-in. cylindrical pellet containing 5.6 wt% platinum on γ -alumina support, was imbedded in a bed of inert α -alumina pellets of similar size to isolate the effect of individual catalyst pellet, and was surrounded by reacting mixture containing saturated cyclohexene vapor. The reaction was run at four different temperatures, i.e. 15, 22, 30 and 40°C, and as a means of changing reaction condition at a given reaction temperature the hydrogen partial pressure was varied. From experimental evidence, two of these multiple steady states were interpreted as the rates in vapor-filled and liquid-filled catalyst pores and the other two steady states as those of pores with different degrees of liquid filling. The transition of phase was apparent from sharp change in observed reaction rate.

Introduction

In the operation of trickle-bed reactors incomplete wetting arises from the partial coverage of packed catalyst particles with flowing liquid stream, especially at low liquid flow rates. The incomplete wetting may be of the following two types. 1) In bed-scale incomplete wetting, some of the particles in the bed are completely covered by the flowing liquid and the remaining particles are covered by the flowing gas; therefore, for each of the packed particles a binary

classification can be made such as liquid-covered particle and gas-covered particle. 2) In particle-scale incomplete wetting, only a part of each packed particle is covered by the flowing liquid. Wijffels *et al.*⁽⁴⁾ measured wetted particle fractions in packed beds of glass beads of various sizes wetted by water and cumene in trickle flow. Their data indicated that particle-scale incomplete wetting was dominant in packed beds of larger particles while in beds of smaller particles bed-scale incomplete wetting was dominant. Analyses of the performance of catalyst particles partially covered by liquid, carried out by several investigators^(1,7,11), led to a fairly comprehensive interpreta-

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tion of the overall performance of trickle-bed reactors wherein particle-scale incomplete wetting was dominant. However, for vapor-covered catalysts the reaction rates were simply interpreted as those of vapor-filled catalyst¹²⁾ or liquid-filled catalyst¹⁰⁾, and no systematic analysis of performance with regard to reaction conditions and properties of the catalyst has been presented to date. A multiplicity of reaction rates associated with change of phase, i.e. liquid to gas phase, have been experimentally observed in trickle-bed reactors as a function of operating parameters such as reactant concentration, gas flow rate and inlet temperature^{2,5,6)}. A detailed description of all the phenomena involved is extremely complex. However, it seems that a detailed description of the phenomena associated with phase transition in a single catalyst pellet covered by a saturated vapor mixture is feasible.

In the discussion below the conceptual ground of the behavior of such catalysts is briefly explained. Catalyst pellets prepared by compressing porous powders usually consist of micropores ($<100 \text{ \AA}$) and macropores ($>100 \text{ \AA}$) and have bimodal pore size distributions. When a highly exothermic reaction takes place in this type of catalyst surrounded by vapor-phase reactants containing a saturated vapor of a liquid, there are regimes of reaction condition in which the catalyst interior is vapor-filled, partially liquid-filled or liquid-filled depending on the past history of the reaction condition. If the reaction is started from the vapor-filled pores and the condition for reaction in pores is changed so as to decrease the reaction rate, the temperature difference between the catalyst and the surrounding bulk will decrease and eventually condensation will begin to take place in micropores of the catalyst due to the increased relative pressure of the condensible gas, defined as the saturation vapor pressure of liquid reactant at the condition of the bulk divided by the saturation vapor pressure of the liquid reactant at catalyst temperature. In this case the reaction rate would be lowered because of the decreases in mass transport rates, intrinsic reaction rates and temperatures between partially liquid-filled catalyst and vapor-filled catalyst, and as a result of the lowered reaction rate the temperature of the catalyst would be further lowered. Consequently, condensation further progresses to larger pores until all the micropores are filled with the condensed liquid. If now the condition is changed to increase the reaction rate, the temperature difference will increase but at first it would still be lower than that of vapor-filled catalyst. As catalyst temperature rises, the liquid in the pores will start to evaporate and eventually vapor phase will prevail in all the pores of the catalyst. The conditions leading to condensation of vapor phase in micropores and those leading to evaporation of the liquid in micro-

pores are different, and this difference may give rise to a set of multiple steady states.

If the reaction is started after all the internal pores are filled with the liquid and the condition is changed to increase the reaction rate, the temperature of the liquid in pores will rise and evaporation will start to take place in the macropores of the catalyst. Here the reaction rate of catalyst may be equal to the rate of vapor-filled catalyst or that of the partially liquid-filled catalyst, depending on the reaction condition at which the evaporation of the liquid begins. But as the reaction condition is further moved in the direction of increasing reaction rate, the reaction rate will surely exhibit the rate of vapor-filled catalyst. Due to large differences between diffusivities of the liquid and the vapor inside the pore structure, the reaction rates of vapor-filled catalyst and liquid-filled catalyst can be very different. In addition, the conditions leading to the filling of the catalyst interior with liquid and evaporation of the liquid are different. Again, these differences can give rise to a steady state multiplicity.

1. Capillary Condensations in a Porous Catalyst

When a highly exothermic heterogeneous catalytic reaction is taking place in a porous catalyst surrounded by reacting materials containing a saturated vapor of a liquid, the Kelvin equation can describe the capillary condensation phenomenon quite adequately because only transfer of matter from one phase to the other phase is occurring at phase boundaries while the reaction is taking place only on the walls of the pores. In this case the relative pressure of a condensible gas is determined as the ratio of saturation vapor pressure at the bulk condition to saturation vapor pressure at the temperature of the catalyst.

$$\ln \frac{P_b}{P_c} = -\frac{2V\sigma}{rRT_c} \cos \phi \quad (1)$$

Here the simplifying assumption, $\phi=0$, is usually made. The relation between temperature and vapor pressure of a liquid is well approximated by a Clausius-Clapeyron type equation:

$$\ln \frac{P_b}{P_c} = -A \left(\frac{1}{T_b} - \frac{1}{T_c} \right) \quad (2)$$

From (1) and (2),

$$A \left(\frac{1}{T_c} - \frac{1}{T_b} \right) = -\frac{2V\sigma}{rRT_c} \quad (3)$$

From a temperature difference between the catalyst and the surrounding bulk arising from the heat of reaction, the corresponding pore radius r_1 can be readily estimated with Eq. (3): the pores with radii up to and including r_1 are filled with the condensed liquid.

Many real porous solids usually exhibit hysteresis in adsorption and desorption processes. Several explanatory theories for this are proposed and well summarized

by Gregg and Sing³). One of them explains the hysteresis in terms of the different shape of the meniscus during adsorption and desorption. During the desorption process the shape of the phase boundary is assumed to be hemispherical while during adsorption the phase boundary is supposed to be cylindrical, i.e. adsorbate multilayer is formed on the pore wall. In this case the Cohan equation should be used for the adsorption process.

$$\ln \frac{P_b}{P_c} = -\frac{\sigma V}{rRT_c} \quad (4)$$

and

$$A\left(\frac{1}{T_c} - \frac{1}{T_b}\right) = -\frac{\sigma V}{rRT_c} \quad (5)$$

In actual pore systems there is already an adsorbed layer on the walls before capillary condensation begins or after evaporation of already condensed liquid takes place, and the thickness of this layer must be taken into account in calculating pore radius.

$$r_p = r + t \quad (6)$$

The thickness of nitrogen at its normal boiling point is relatively well characterized but for most organic vapor systems the estimation of thickness usually requires an additional experiment to measure the adsorption isotherm on a non-porous substance. Here the thickness is estimated for cyclohexane with the assumption that the number of the molecular layers can be approximated by the Halsey equation developed for nitrogen adsorption and the average thickness of a single adsorbed molecular layer estimated by the method discussed by Gregg and Sing.

$$t = 5.1 \times 10^{-8} \left(\frac{5}{\ln(P_c/P_b)} \right)^{1/3} \quad (7)$$

The relations between temperature difference and the estimated pore radius for adsorption and desorption of cyclohexane vapor at 22°C are given in Fig. 1. The points obtained for cyclohexane and mixture of cyclohexene and cyclohexane fall on the same curve due to the similarity of the two compounds in physical properties. The value of pore radius estimated for a given temperature difference or, conversely, the temperature difference estimated for a given pore radius would be just an indication of the magnitude expected, as discussed by Gregg and Sing.

2. Experimental Apparatus and Procedures

In this study the multiple steady states were experimentally observed by hydrogenating cyclohexene on a Pt/Al₂O₃ catalyst prepared in this laboratory. A schematic diagram of the experimental apparatus is shown in Fig. 2.

A mixture of hydrogen and nitrogen gases, metered separately, flows through a deoxygenator (D) to re-

Fig. 1 Temperature difference vs. pore radius

Fig. 2 Experimental apparatus

move trace oxygen which is known to affect the activity of the platinum catalyst. The sum of the two flow rates is always adjusted to 500 ml/min at 16°C and 1 atm. After drying (E), it is passed through a saturator (G) filled with cyclohexene and heated slightly above the reaction temperature to prevent under-saturation. Any supersaturation is removed in a condenser (F) before the reactants enter the reactor (J). The temperatures of the condenser (F) and the reactor (J) are controlled by means of water circulated from a constant-temperature bath (B). The reactor is made of 28.3 mm I.D. Pyrex glass in which, to isolate the effect of individual catalyst pellet, the catalyst pellets are imbedded a large distance away from each other in a bed of inter α -alumina pellets of similar size. One or two catalyst pellets are used in rate measurement of vapor-filled and partially liquid-filled catalyst, and five catalyst pellets in rate measurement of liquid-filled catalyst. The reactor effluent stream is condensed in a trap (K), and analyzed by gas chromatography. The catalysts are in the form of cylindrical pellets 4.6 mm in diameter and 4.8 mm in length, containing 5.6 wt % platinum on γ -alumina support, and are prepared by the incipient wetness technique using chloroplatinic acid solutions. The porosities and pore size distribution of the catalyst were measured by nitrogen adsorption and mercury penetration. Figure 3 shows the pore size

Fig. 3 Pore size distribution

Fig. 4 Dependence of temperature difference on hydrogen partial pressure at each reaction temperature

distribution, and clearly indicates a bimodal distribution characteristic of pellets made by compressing porous particles. The platinum dispersion of the catalyst measured by the well-known hydrogen pulse chemisorption technique was 70.2%. In Table 1 the properties of the catalyst and α -alumina pellet are listed. The reaction condition was varied by means of the hydrogen partial pressure in the reactant mixture, and the ratio of the hydrogen and the nitrogen flow rates effectively determined the hydrogen partial pressure. The reaction was run at atmospheric pressure and at four different temperatures, 15, 22, 30 and 40°C.

3. Experimental Results and Discussion

3.1 Catalyst pretreatment and reproducibility of measurements

When a fresh sample of catalyst pellets was charged, the catalyst was activated at 200°C under a small hydrogen flow for at least 3 hours. The catalyst pellet once activated showed no loss in activity throughout the duration of experiments done with it. A catalyst pellet previously exposed to reactant mixture was pretreated in air at 300°C for 0.5 hour before being placed in the reactor to remove the carbonaceous material which might be deposited in the catalyst interior.

Under the same reaction conditions, the deviations

Table 1 Properties of catalyst and α -alumina pellet

Catalyst pellet	
Size	4.6 mm (diameter) by 4.8 mm (length) cylindrical pellet
Average pellet weight	0.1157 g
Solid density	3.77 g/cm ³
Pellet density	1.45 g/cm ³
BET surface area	170 m ² /g
Total pore volume	0.424 cm ³ /g
Void fraction	
micropore	0.528
macropore	0.0878
Mean pore radius	
micropore	36 Å
macropore	1460 Å
Platinum content	5.6 wt %
Platinum dispersion	70.2 %
α -Alumina pellet	
Size	4–5 mm spherical pellet
Pellet density	1.92 g/cm ³
Surface area	3–20 m ² /g

Table 2 Classification of activity

Catalyst	reaction condition : 30°C, 654 mmHg P_{H_2}			Activity
	Weight [g]	No of pellet	Rate $\times 10^2$ [mol/g-cat·hr]	
C1	0.2463	2	9.88	low
C2	0.1141	1	9.80	low
C3	0.1131	1	9.65	low
C4	0.1197	1	11.5	high
C6	0.1012	1	12.1	high
C7	0.1176	1	13.5	high
C9	0.1162	1	12.0	high
C10	0.2488	2	10.8	medium
C11	0.1145	1	11.2	high

mean = 11.17
standard deviation
= 1.29 (12%)

in measured reaction rates were always less than 10% and the mean was calculated as 4.5%. Reaction rate variations of about 9% due to the effect of packing arrangement of inert pellets around a catalyst pellet on the external mass and heat transport were observed when the bed was repacked several times. However, the measured rates varied much more for different samples of the catalyst, up to 20% deviation.

The catalyst samples were tested at a chosen condition (30°C, 654 mmHg P_{H_2}) and were divided into three levels of activity, i.e. high, medium and low, as listed in Table 2. Because of the different influences of external transports on reaction rate resulting from the random nature of the packing process of the bed, the classification of catalyst in Table 2 may possess some arbitrariness.

3.2 Vapor-filled catalyst

As stated previously, the temperature difference between the catalyst pellet and the surrounding stream needs to be high to prevent capillary condensation in the pores of the catalyst. The temperature differences were measured by winding a chromel-alumel thermocouple wire (A'W'G' 24) on a catalyst along the lateral direction. Figure 4 shows this result. Since thermal

conductivity of nitrogen is about one-tenth that of hydrogen, the heat transport resistance around a catalyst will decrease as the hydrogen partial pressure increases in the reactant mixture surrounding the catalyst. This is the reason for the smaller temperature differences observed in spite of increasing reaction rate. The bed temperature measured along the longitudinal direction through the thermowell in the reactor showed 2–10°C variations. It is quite clear that there is significant axial and radial heat conduction around the catalyst when the catalyst is overheated due to high heat of reaction, about 28 kcal/mole. Using the rates of heat transfer calculated by the use of heat of reaction, along with measured reaction rates and temperature differences, the heat transfer coefficients or the Colburn j factors, j_h , incorporating the effects of axial and radial heat conductions were calculated.

Regression analysis of these values with the measured bed porosity ($\varepsilon=0.42$) produces the following relation between j_h and Re_p with a mean deviation of 23% in a Reynolds number range of 1.5 to 11.

$$\varepsilon j_h = 4.92 Re_p^{-0.755} \quad 1.5 < Re_p < 11 \quad (8)$$

Vast numbers of studies reported in the literature on heat transfer in packed beds are on fluid-to-particle heat transfer by convection. Recently Gupta *et al.*⁴¹ reexamined 940 experimental data on fluid-to-particle heat transfer reported in the literature and rerelated them by the following formula:

$$\varepsilon j_h = \frac{2.876}{Re_p} + \frac{0.3023}{Re_p^{0.35}}, \quad 10 < Re_p < 10,000 \quad (9)$$

Comparing the two relations above one notes that Eq. (8) yields appreciably higher values of heat transfer coefficient than does Eq. (9). The difference between these two relations seems attributable to the contribution of axial and radial heat conduction in the bed. However, in the higher Reynolds number region these conduction effects are expected to be negligible.

With increasing gas flow rate the reaction rate of the vapor-filled catalyst always increased in the limited experimental range of 100–500 ml/min. From this observation and the measured temperature differences it is evident that mass and heat transfer resistances were significant around the catalyst exhibiting the rates of vapor-filled catalyst.

At temperatures of 22 and 30°C, all the catalyst samples were tested and the resulting curves of the rate data form parallel lines according to the level of activity over wide ranges of hydrogen partial pressures as shown in Figs. 5 and 6. The slopes of these lines are very small compared with the trend expected from kinetic studies of vapor-phase cyclohexene hydrogenation^{8,13} in which the rate is known to exhibit an order of 0.5 to 1 with respect to hydrogen pressures. Again, these small increases in reaction rates imply the

Fig. 5 Reaction rate of vapor-filled catalyst (22°C)

Fig. 6 Reaction rate of vapor-filled catalyst (30°C)

Fig. 7 Reaction rate of liquid-filled catalyst

existence of appreciable external transport resistances in and around the catalyst, and further imply that the limiting reactant is cyclohexene.

3.3 Liquid-filled catalyst

To induce condensation in the catalyst interior, the catalyst pellets were contacted with a nitrogen stream saturated with cyclohexene vapor before reaction started. After this step a series of runs were made by increasing hydrogen partial pressure in small increments until evaporation of liquid in pores took place.

Since the evaporation was always accompanied by a sharp increase in reactor bed temperature and conversion of cyclohexene, this phenomenon was easily noticed. Reaction rates at each temperature are plotted together in Fig. 7. Throughout the measurements, no bed temperature increase as high as 0.1°C was observed except on the occasion of evaporation. The measured rates did not change with varying gas

Fig. 8 Multiple steady states due to condensation in micropores (low activity)

Fig. 9 Multiple steady states due to condensation in micropores (medium activity)

flow rate of 100–500 ml/min. From these observations, together with the criterion of Mears⁹⁾, it is clear that the rate data of liquid-filled catalyst were obtained in the absence of external mass and heat transport effects. The apparent activation energy calculated from an Arrhenius plot of rate constants was 5.96 kcal/mol. If solubilization rate of hydrogen at the catalyst external surface is very rapid compared to the rate of dissolved hydrogen transport into the catalyst interior, the rates obtained in this manner will correspond to the rate measured in the CSTR usually employed in the study of liquid-phase catalytic hydrogenations in which the catalyst pellets are placed in a basket-type impeller to minimize the effects of external transport resistances.

The temperature difference between the catalyst and the surrounding medium just before the evaporation is estimated with the heat transfer correlation (8) and is listed in Table 3. The estimated values show good agreement between them, but the pore radii estimated from Eq. (3) are somewhat lower; that is, the estimated temperature difference needed to evaporate the liquid in pores is slightly higher than the expected value corresponding to macropores of the catalyst. This small discrepancy can be attributed to a small degree of supersaturation of cyclohexene. About 1% supersaturation in the mixture may not introduce appreciable error in measured rates, but it may be critical in capillary condensations in macropores since in this

Table 3 Evaporation temperature difference and corresponding pore radius

Bulk temp [°C]	Rate $\times 10^3$ [mol/g-cat·hr]	P_{H_2} [mmHg]	T [°C]	r [Å]
40	1.29	76.8	0.49	1000
30	1.53	123	0.49	1000
22	1.64	191	0.47	1000

region a small change in temperature difference or in P_b/P_c (relative pressure) causes an abrupt change in calculated pore radius, as can be seen in Fig. 1. It may be noted here that the vaporization of liquid in macropores leads to another reaction state in the catalyst.

3.4 Partially liquid-filled catalyst

The results of measurement with a low activity catalyst C1 are shown in Fig. 8. With decreasing hydrogen partial pressure the rate decreases slowly to a level of 0.03 mol/g-cat·hr, and when hydrogen partial pressure has reached below about 43 mmHg, the rate drops suddenly to a level of 0.01 mol/g-cat·hr.

If the hydrogen partial pressure is further lowered the rate decreases further and follows branch C in Fig. 8. If the hydrogen partial pressure is increased, the rate increases again, running along branch C, and above 87 mmHg hydrogen pressure it suddenly jumps to branch B.

At this point, with increasing or decreasing hydrogen partial pressure the reaction rate increases or decreases, running along branch B, and finally with increasing hydrogen partial pressure the rate jumps from branch B to branch A above 240 mmHg hydrogen pressure.

Due to experimental difficulties, some of the extreme points indicated by the dotted lines were not obtained although the tendency toward their existence is beyond doubt.

The important fact to be noted here is that external mass and heat transfer plays a key role in this multiplicity of reaction rate.

In experiments with higher-activity catalyst, i.e. medium-activity catalyst C10, the range of occurrence of multiple steady states was narrower and the corresponding range of multiple steady states of branches B and C in Fig. 8 nearly vanished. Figure 9 shows the results, and only a single hysteresis loop seems to appear in it. In the results obtained with an even higher activity catalyst, the hysteresis loop seemed to vanish. The catalyst which exhibited the rates of branch B and branch C always exhibited those of branch A in the course of experiments when the reactor was purged with gas mixture, hydrogen and nitrogen, or inert gas free from liquid reactant vapor for about 10 minutes, and the reaction was started again. These observations clearly indicate that the catalysts exhibiting the rate of branch B and C contained condensed reactants in part of their interior pores, and moreover

the degree of condensation in the interior would be higher along branch C than along branch B.

Conclusion

It is fairly obvious from the experimental results that as the relative pressure of condensible gas at the condition of catalyst interior increases, condensation occurs from small pores, and the phase of the catalyst interior can be different from that of the bulk surrounding the catalyst. In this work it can be seen that vapor, liquid or both phases can exist in the interior of the catalyst surrounded by reacting materials containing a saturated vapor of a liquid depending on the reaction condition and its history, thereby making possible hysteresis loops of reaction rate with respect to reaction condition. The degree of condensation can be estimated as a function of the temperature difference between the catalyst and the ambient stream according to the changing direction of reaction condition, i.e. condensation in vapor-filled pores and evaporation in liquid-filled pores.

Thus the simple interpretation of the reaction rates of vapor-covered catalyst pellets in trickle bed reactors as those of liquid-filled catalyst or vapor-filled catalyst can lead to erroneous analysis on the overall performance of trickle bed reactors in which bed-scale incomplete wetting is occurring.

This work is restricted to a single kind of porous pellet having bimodal pore size distribution, and it would be helpful to try other types of porous material.

Nomenclature

A	= constant in a temperature vs. vapor pressure relation	[°K]
P_c	= saturation vapor pressure of condensible gas at bulk temperature	[mmHg]

P_b	= saturation vapor pressure of condensible gas at catalyst temperature	[mmHg]
R	= gas constant	[erg/mol·°K]
r	= pore radius	[cm]
r_p	= pore radius corrected with adsorbed layer thickness	[cm]
T_b	= bulk temperature	[°K]
T_c	= catalyst temperature	[°K]
t	= adsorbed layer thickness	[cm]
V	= molar volume	[cm ³ /mol]
ε	= bed porosity	[—]
σ	= surface tension	[dyne/cm]
ϕ	= contact angle	[deg.]

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