

THE ROLE OF PARTIAL INTERNAL WETTING IN HYSTERESIS BEHAVIOR OF CATALYST PELLET

F. A. Hessari

Materials and Energy Research Center

P.O. Box 14155-4777 Tehran, Iran, merc88@iran.com

(Received: April 20, 1998 - Accepted: January 15, 2000)

Abstract The phenomenon of capillary condensation is studied through the weight change of condensed phase in an internally wetted porous pd catalyst pellet during the course of exothermic reacion of cyclohexane hydrogenation in a thermogravimetric analyzer (TGA). The direct measurement of condensed phase indicates that evaporation of condensed phase is confined to the macropores of catalyst pellet at the lower limit of reaction rate. Phase transition from lower to upper limit reaction rate associates with the sharp temperature rise in the catalyst pellet. A substantial fraction of pellet pores volume opens in the phase transition and evaporation of condensed phase extends to the micropores of catalyst pellet. The TGA studies shows the reacion rate multiplicities is the result of condensation - evaporation hysteresis associated with the internally wetted catalyst pellet.

Key Words Multisteady States, Partial Internal Wetting, Phase Transition, Steady State Multiplicity

Three phase reactors consist of gas, liquid and solid phases and are commonly used for hydrogenation, hydro-desulfurization, denitrogenation, along with a variety of other catalytic reactions. Incomplete wetting of catalyst bed is reported to be associated with the operation of three phase reactors. This incomplete wetting is generally attributed to poor liquid distribution. However, in the cases involving high heats of reaction, incomplete wetting occurs due to volatility of reactants and products, mass transport effects and hydrodynamics of flow.

INTRODUCTION

Three phase reactors consist of gas, liquid and solid phases and are commonly used for hydrogenation, hydro-desulfurization, denitrogenation, along with a variety of other catalytic reactions. Incomplete wetting of catalyst bed is reported to be associated with the operation of three phase reactors. This incomplete wetting is generally attributed to poor liquid distribution. However, in the cases involving high heats of reaction, incomplete wetting occurs due to volatility of reactants and

products, mass transport effects and hydrodynamics of flow.

The studies of Hankia et al. (1) indicated such complexity in the behavior of their laboratory trickle bed catalytic reactor. It was shown that under certain conditions cyclohexene hydrogenation over the bed of Pd catalyst pellets, the liquid mixture in the trickle bed reactor could evaporate (externally dry condition) as a result of the heat liberated by the reaction. Evaporation of the liquid phase at some point in the bed brings more direct contact between gas and the solid catalyst and

hence, leads to a sharp increase in reaction rate.

Some single catalyst pellet studies, both experimental and theoretical have addressed the issue of partial internal wetting of catalyst pellets [2-4]. These studies have not taken into account the combined effects of reaction exothermicity, vaporization of condensed phase and transport of reacting species.

Partial wetting of the catalyst particle may be external or internal. In the former case, a fraction of external surface of the particle is wetted by the flowing liquid. In partial internal wetting, a portion or complete volume of catalyst pellet is filled by the liquid. Internal wetting is thus brought about by capillary action in porous catalyst, and due to the strong capillary forces complete filling of pores is caused by liquid imbibition. But with volatile liquid phase in exothermic reaction condition, a situation arises where catalyst pellet is externally dried but internally wetted by condensed phase [5-7]. However, quantitative data in this area is limited.

In order to gain insight into the behavior three phase reactors and the formation of hot spots under non isothermal reaction conditions with volatile liquid phase, it is necessary to elucidate the phenomena of partial internal wetting in particle scale at the single pellet level. This is the prime objective of this work.

THEORETICAL CONSIDERATION IN INTERNAL WETTING PHENOMENON

In general, the Kelving and Cohan [8] Equations 1 and 2 are used to describe capillary evaporation and condensation of condensable vapor in porous media.

$$\ln (P/P_0) = - \frac{2 s V}{R T r_m} \quad (1)$$

$$\ln (P/P_0) = - \frac{s V}{R T r_m} \quad (2)$$

Where P_0 is vapor pressure, s surface tension ,

V specific volume and T the adsorbent temperature and r_m mean radius of curvature.

$$\frac{2}{r_m} = \frac{1}{r_1} + \frac{1}{r_2} \quad (3)$$

in which r_1 and r_2 are two principal radii of the curved meniscus. Liquid and gas phases are in equilibrium at the meniscus of the liquid.

In the catalyst interior, the wet portion is referred to the pores that are filled with condensed liquid to the gas filled pores. The phase transition occurs between liquid filled (wet) and gas filled (dry) conditions. Evaporation and condensation are therefore associated with the phase changes in catalyst pores. The vapor liquid interface shape varies in the two extreme cases of evaporation and condensation. Evaporation starts from filled pores with hemispherical vapor-liquid interface shape, for which r_m can be related to the radius of the cylindrical pore r by

$$r_m = r \sec (\theta) \quad (4)$$

where θ is the contact angle. For perfectly hemispherical meniscus $\theta = 0$ and $r_1 = r_2 = r$ so that $r_m = r$.

Condensation occurs in empty pores with a cylindrical vapor-liquid interface for which $r_1 = r$ and $r_2 = \infty$.

This leads to

$$r_m = 2r \quad (5)$$

Owing to these differences, condensation and evaporation do not retrace each other on the same path, so that hysteresis effect is associated with the transport of species in the condensed phase and leading to multisteady state situation.

CATALYST PREPARATION

Wet impregnation technique was used for loading of palladium on γ - alumina support. The required amount of palladium chloride salt

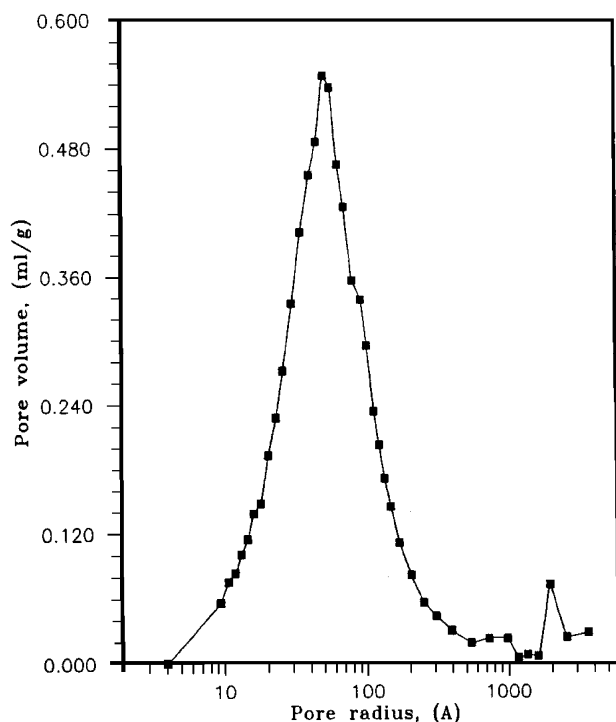


Figure 1. Pore size distribution data of Pd catalyst pellet.

(59-60 percent w/w Pd) was dissolved in a small volume of hydrochloric acid. The support material was soaked in this solution at the temperature of 30°C under vacuum. The calcination temperature of the catalyst was at 380°C. The catalyst pellet was reduced under hydrogen gas at a temperature of 200°C for 8 hours prior to hydrogenation reaction.

Figure 1 shows pore volume versus pore size data for the catalyst pellet using both the nitrogen adsorption and mercury porosimetry techniques. The nitrogen adsorption data are used to calculate pore size distribution up to the 543 Å and mercury porosimetry for data above the 543 Å. Table 1 summarizes the physical properties of this pellet. The catalyst pellet is found to have a surface area of 144.8 m²/g and is characterized by an average pore radii of 41.1 Å (mesopores), 1500 Å (macropores) and the total pore volume of 0.389 ml/g.

MATERIALS AND METHODS

The cyclohexane was of high purity (Fluka;

> 99.0 percent). It was treated in a column of γ-Al₂O₃ to remove any peroxide prior to experiments. The high purity nitrogen and hydrogen (> 99.0 percent v/v) were further purified by passing through deoxygenation. The spherical γ-Al₂O₃ catalyst support was used in this study.

The composition of reaction mixture was analyzed by gas chromatography. A 15 percent w/w Carbowax column (stationary phase) of 2.0 m length was used to analyze the cyclohexane and cyclohexane retention time are about 1.09 and 1.63 min at the oven temperature of 3°C and 30 ml/min of nitrogen as a carrier gas respectively. The temperature of injection port was set at 110°C.

EXPERIMENTAL APPARATUS AND PROCEDURE THERMOGRAVIMETRIC ANALYZER (TGA)

A schematic diagram of TGA experimental setup is shown in Figure 2. The experimental setup consisted of DuPont 951 Thermogravimetric Analyzer (TGA), gas saturator, condenser, constant temperature bath, Brooks electronic metering system (Model 5850 Flow Controller), deoxygenation column, drying column and IBM DS/2 data acquisition system. The TGA accuracy of the weight measurement is of the order of 0.005 mg. The Brooks Flow controller has an accuracy of 2 percent of the full scale.

The reaction chamber was attached to the thermogravimetric analyzer, in which 0.5 percent Pd catalyst pellet was suspended from the quartz rod arm of side-loading balance. The purified gas after passing through deoxygenation unit and molecular sieve column, was bubbled through cyclohexane in the saturator. Any supersaturation was removed from gases by a condenser at the bath temperature before entering the reactor. The weight change and the temperature of catalyst

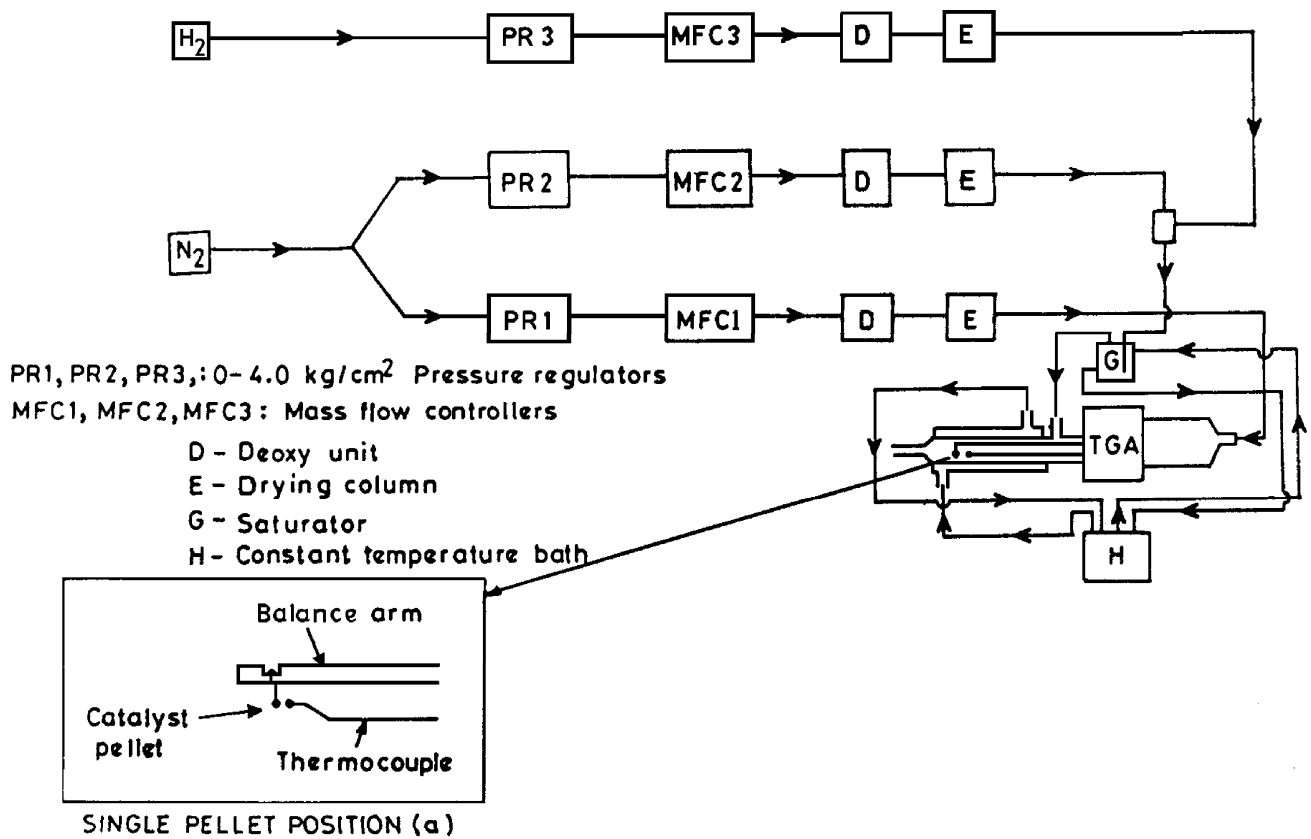


Figure 2. TGA Experimental setup.

particle were monitored continuously by the data collection interface and recorded on an IBM computer. The frequency of data collection was high (1 data point per 3 second) permitting the data to be represented by the continuous curves. The connecting pipe between the saturator and reactor was slightly heated to avoid any condensation of cyclohexane. A small flow of purified nitrogen gas at 5 ml/min was purged in the rear section of the balance chamber in order to prevent diffusion and condensation of reactor gases on the balance interior parts.

In the first, the entire weight of holder and catalyst pellet was tared before introducing the saturated nitrogen gas with cyclohexane to the reaction chamber of TGA, so that any weight gain directly represented the amount of the condensed phase in the pellet. Hence, condensation of cyclohexane in the catalyst

pellet could be directly monitored by the Thermogravimetric Analyzer (TGA). A fixed flow of nitrogen gas was bubbled through cyclohexane in the saturator hold at desired constant temperature. The saturated nitrogen gas was then introduced to the reaction chamber containing catalyst pellet.

When the entire volume of the catalyst pellet was filled by condensed cyclohexane no further weight gain in the pellet was recorded by the TGA. The reaction was then started by introducing hydrogen gas into the flow of nitrogen gas and sum of the two flows was always kept constant. The reaction condition was then changed by gradually increasing hydrogen flow rate in order to increase the reaction rate. As a result, due to temperature rise in a catalyst pellet, evaporation of the condensed liquid initially took place in the macropores with a small variation in the amount

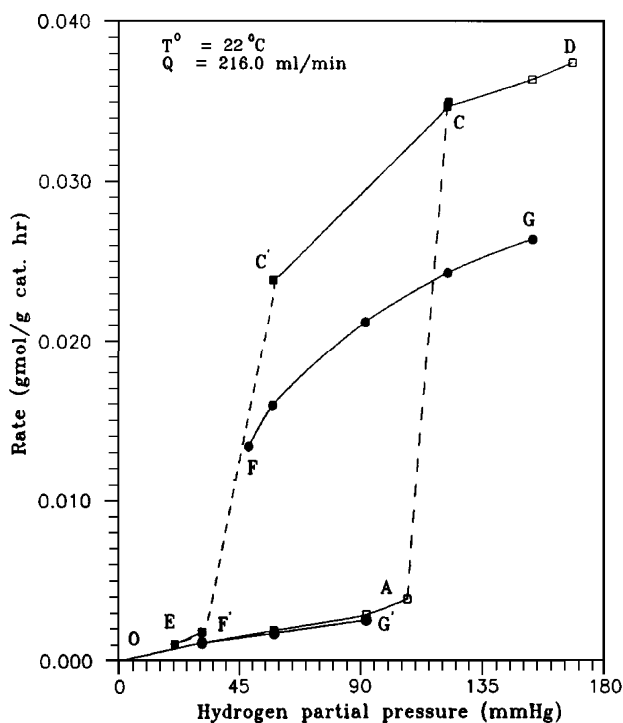


Figure 3. Variation of reaction rate with hydrogen partial pressure in TGA.

of condensed phase in the pellet. The low reaction rate corresponded to the predominantly liquid filled pores (OA branch of Figure 3). The effluent gas stream from reactor was analyzed for cyclohexane content by the gas chromatography to calculate the reaction rate. As the reaction condition (hydrogen flow rate) was further changed to increase the reaction rate, the evaporation of the condensed liquid was extended to the micropores of catalyst pellet so that the catalyst pellet exhibited high reaction rates corresponding to predominantly vapor filled pores (CD branch of Figure 3).

In the predominantly vapor filled state, the hydrogen flow rate was gradually reduced to decrease the reaction rate (DC branch of Figure 3). Consequently, the temperature difference between the catalyst pellet and the reactor jacket was decreased and eventually condensation of cyclohexane began in the pores of catalyst. The reaction rates correspond to those of predominantly liquid filled state under

this condition (C E branch of Figure 3).

In the second step of the experiment, the catalyst pellet was purged with nitrogen gas in order to remove condensed liquid from the catalyst pores before introducing hydrogen gas into the system. The same cycle of experiment is repeated for gas prefilled catalyst pellet.

The overall result of the complete experimental cycle was plotted as a reaction rate, temperature rise of catalyst pellet and weight change of condensate, as versus hydrogen pressure. Experiments are carried out at the atmospheric pressure but the sum of the two flow rates of hydrogen and nitrogen is always kept constant during the course of experiment. The weight of catalyst pellet was 0.0743 g for the single pellet experiments. The same catalyst pellets were used in all experiments performed.

EXPERIMENTAL RESULTS

The TGA experiments were carried out to establish the role of partial internal wetting in a porous catalyst surrounded by reacting mixture saturated with cyclohexane vapor during the hydrogenation of cyclohexane. The phenomenon of capillary condensation and its associated effect on reaction rate are studied through weight change of condensed phase in the catalyst pellet under steady state reaction condition. The design of experiment represented the case where the liquid phase is a volatile limiting reactant. The weight change and temperature of catalyst pellet were recorded during the course of the exothermic reaction.

Two sets of experiments were performed at flow rate of 216.0 ml/min and bulk temperatures of 15 and 22°C. In the following section, the experimental results are presented as a plot of reaction rate, temperature rise of the catalyst pellet with respect to bulk and weight change of condensed all versus hydrogen partial pressure.

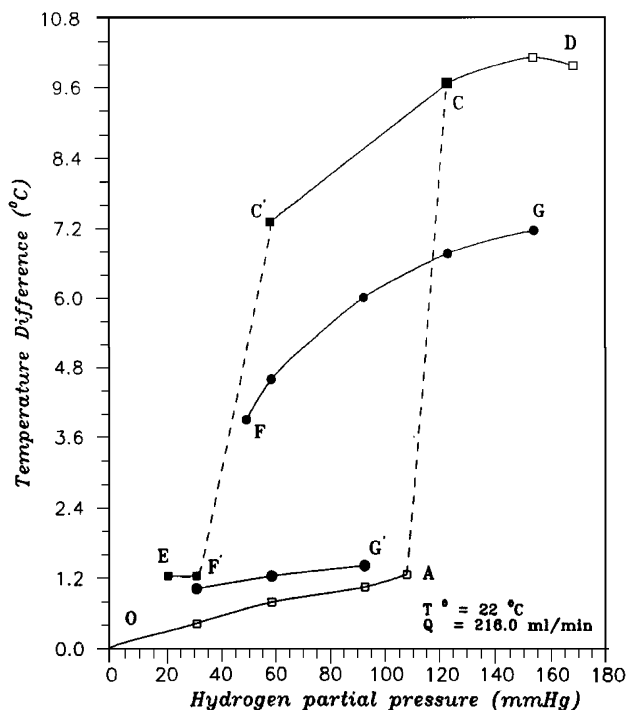


Figure 4. Variation of catalyst temperature with hydrogen partial pressure.

LOWER LIMIT REACTION RATE

Figure 3 shows the observed reaction rate versus hydrogen partial pressure at the bulk temperature of 22°C and flow rate of 216.0 ml/min. The branch OA in Figure 3 represents the lower limit of exhibited reaction rate in which a substantial volume of catalyst pellet is filled by condensed liquid. As shown in Figure 4A, the maximum temperature rise of catalyst pellet is observed to be 0.83°C with respect to the jacket temperature at this branch. Along this branch, 1.33 mg of condensed liquid is evaporated from the catalyst pores, as it is measured by TGA in Figure 5. This shows that a large fraction of catalyst pore volume is filled by condensed phase at lower branch OA. It is seen that evaporation of condensed liquid is confined to the macropores of catalyst at the lower branch reaction rate.

Figure 5 also shows that the initial uptake of pellet, when it is purged with nitrogen gas saturated with cyclohexane, is 19.5 mg before

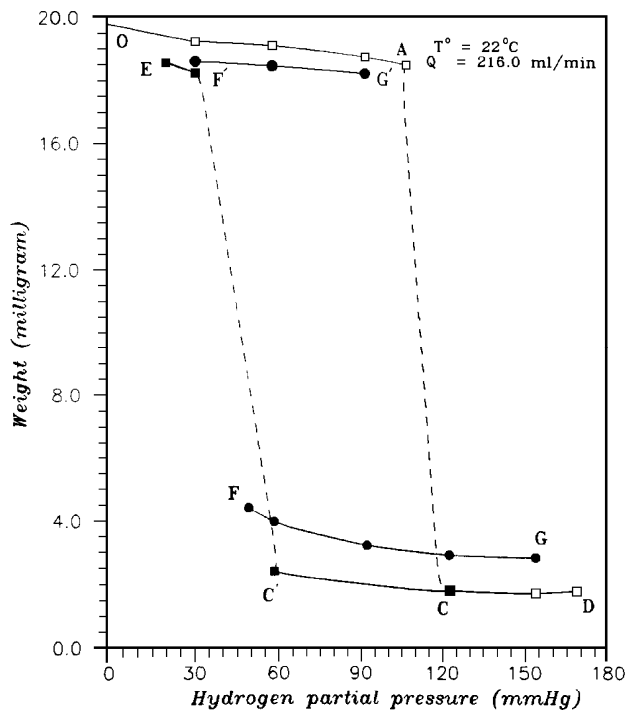


Figure 5. Variation of condensed liquid amount in catalyst pellet with hydrogen partial pressure.

the reaction starts by introducing hydrogen gas into the system. The wetted pore volume of catalyst pellet can be calculated from the weight and density of condensate in the catalyst pores. The wetted pore volume of catalyst pellet is calculated to be 0.350 ml/g based on the 19.5 mg uptake of cyclohexane with the average density of 0.7948 g/ml at 22°C. Since the density of cyclohexane and cyclohexane are very close to each other, their value is used for calculating the wetted pore volume of catalyst pellet.

The total pore volume of catalyst pellet using the nitrogen adsorption and mercury porosimetry techniques was 0.389 ml/gm, as shown in Table 1.

The filled pore volume of pellet is calculated to be 0.350 ml/g cat. from TGA observation. This is less than the total pore volume of pellet which is 0.389 ml/g. This could be due to the macropores in the catalyst pellet which can not be filled by the mechanism of capillary condensation and existence of fine pores in the

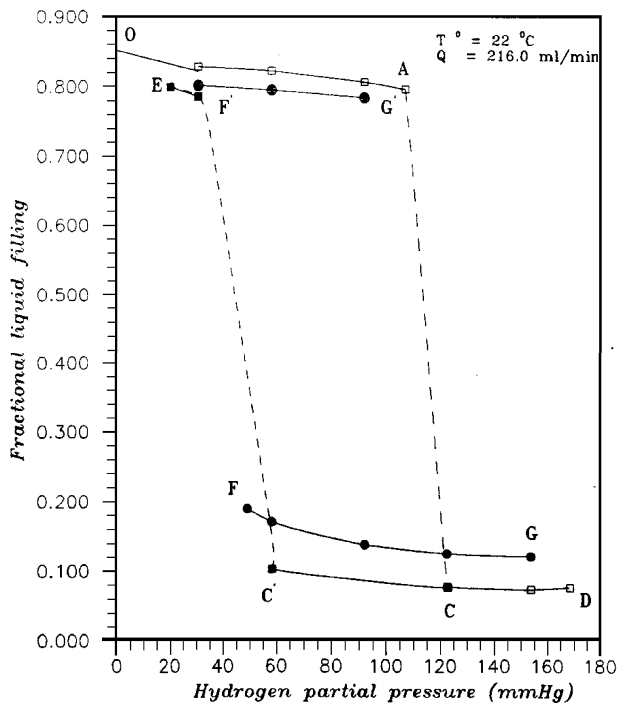


Figure 6. Variation of catalyst pellet fractional wetting with hydrogen partial pressure.

catalyst pellet in which mechanism of filling is different from that of capillary condensation [8].

The fractional liquid filling of catalyst pellet is then calculated as the ratio of wetted pore volume to the total pore volume of catalyst pellet and is shown in Figure 6. The total pore volume is taken to be 0.389 ml/g in calculating the fractional liquid filling of catalyst pellet. As shown in Figure 6, the fractional liquid filling reduces to a value of 0.795 at point A along the branch OA. A substantial catalyst pore volume is filled by the condensed phase and the reaction rate corresponds to predominantly liquid filled pores at this branch.

UPPER LIMIT REACTION RATE

The reaction rate is suddenly increased from 0.0038 gmol/gm cat, hr at point A to a 0.0347 gmol/gcat hr at point C, as shown in Figure 3. This brings about ten folds increase in the observed reaction rate. This is associated with a temperature rise of 8.41³C with respect to pellet

temperature at point A where 16.68 mg of the condensed liquid is evaporated form the catalyst pores , as shown in Figures 4 and 5 respectively.

Figure 6 shows that the fractional liquid filling of catalyst pellet changes from predominantly liquid to predominantly gas filled state as the catalyst pellet exhibits reaction rate corresponding to CD branch. This shows a phase transition from partially liquid to partially gas filled in the state of catalyst pellet. This observation indicates that the steady states of catalyst pellet corresponds to different degrees of catalyst internal wetting during the course of reaction at different reaction rate branches. The fractional liquid filling reduces to 0.077 at point C on the branch CD and remains constant with further increase in hydrogen partial pressure.

The hydrogen partial pressure is then gradually decreased from point D in Figure 3. The observed reaction rates are shown along the branch DCÆ in Figure 3. The observed reaction rates reduce along this branch to 0.023 gmol/gmcat hr at point C before transition to the lower branch OA. With decrease of hydrogen partial pressure, the catalyst pellet temperature reduces and the condensation initially begins in the finer pores of catalyst pellet and gradually develops in the larger pores at low hydrogen partial pressure. The fraction of liquid filling increases from 0.076 to 0.799 along the branch DE in Figure 6 and as a result, the catalyst pellet finally exhibits lower branch reaction rate at point E in Figure 3.

MIDDLE BRANCH REACTION RATE

Following this experiment and completion of the last cycle experiment (branch DCÆ) on the point E, catalyst pellet is then again purged with nitrogen gas in order to remove the condensed liquid from the catalyst pores. Upon introducing hydrogen gas saturated with cyclohexane into the reaction chamber where the catalyst pores are gas prefilled, the catalyst pellet exhibits the

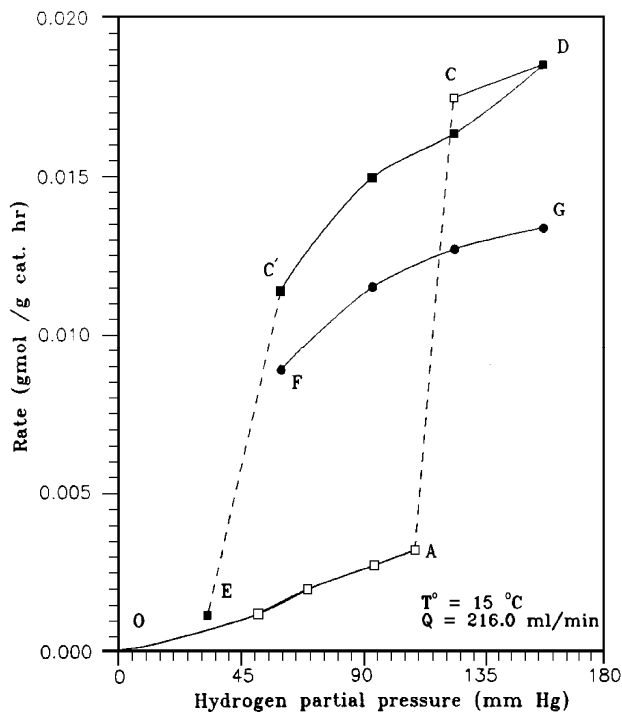


Figure 7. Variation of reaction rate with hydrogen partial pressure.

reaction rates corresponding to the branch FG in Figure 3. In this branch, condensation occurs simultaneously during the course of reaction when hydrogen gas saturated with cyclohexane is introduced into the reaction chamber. The initial uptake of catalyst pellet is recorded to be 4.4 mg at the point F in Figure 5. As hydrogen partial pressure increases along the branch FG in Figure 5, 1.58 mg of condensate is evaporated. A maximum temperature rise of 7.1°C is observed between catalyst pellet and the bulk at the point G. The extent of catalyst pellet pore wetting is different along the branch FG and as a result, catalyst pellet exhibits different reaction rate from the observed reaction at lower and upper branches. This indicates the effect of catalyst internal wetting and its past history on reaction rate multiplicity.

Figure 6 shows that fractional liquid filling varies from a value of 0.189 to 0.121 along the branch FG. It is also observed that if hydrogen partial pressure is set at a low value, due to low

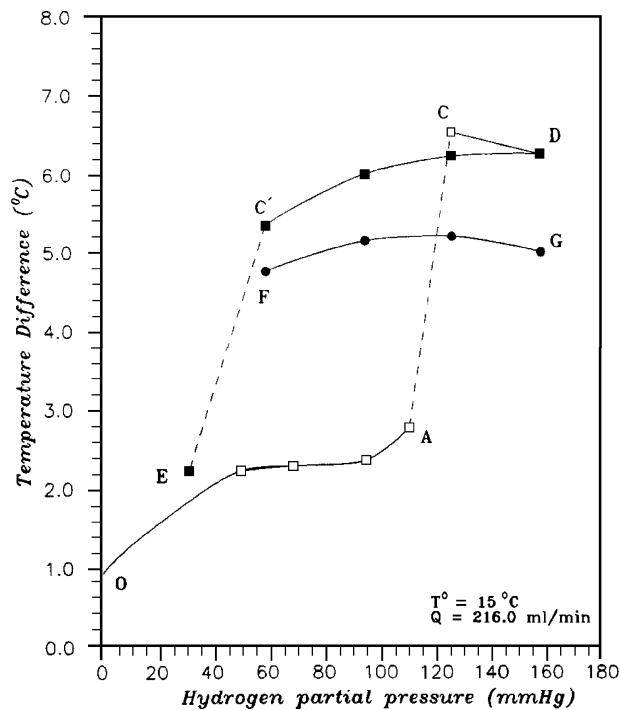


Figure 8. Variation of catalyst temperature with hydrogen partial pressure.

reaction rate, which causes lower temperature difference between catalyst pellet and surrounding, the condensation of condensable species in reacting mixture takes place in the entire pore volume of catalyst pellet. Under this situation, the observed reaction rate (FAG branch of Figure 3) gradually decreases and ultimately corresponds to the lower reaction rate branch OA of Figure 3. This indicates that there is an optimum temperature difference between catalyst pellet and its surroundings in which the catalyst pellet exhibits the reaction rate corresponding to branch FG.

COMPARISON OF BEHAVIOR AT DIFFERENT CONDITIONS

The other set of experiments is performed at flow rate of 216.0 ml/min and with the surrounding temperature of 15°C . Figure 7 shows the observed reaction rate versus hydrogen partial pressure. The branch OA of Figure 7 represents the lower limit of the

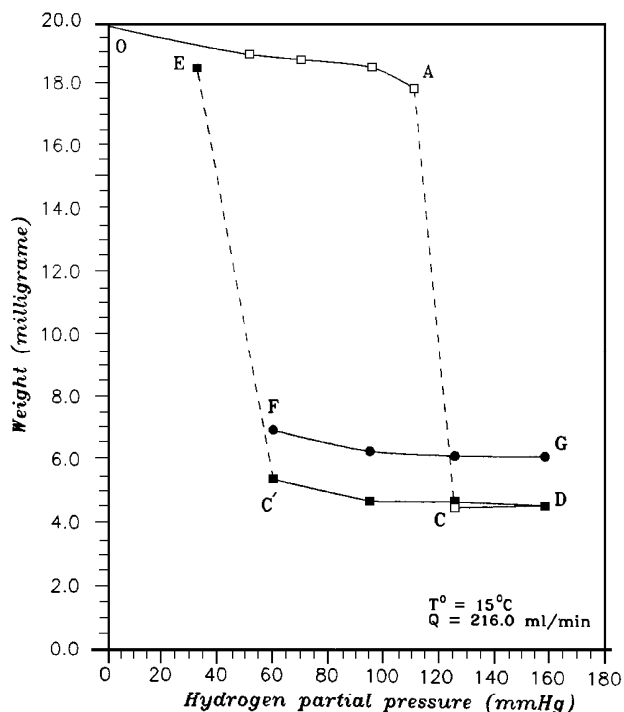


Figure 9. Variation of condensed liquid amount in catalyst pellet with hydrogen partial pressure.

reaction rate where a large fraction of catalyst pore volume is filled with the condensed liquid. The lower branch reaction rate is extended over 110 mmHg of hydrogen partial pressure at the surrounding temperature of 15³C as compared with Figure 3 at the surrounding temperature 22³C. The maximum temperature rise of 2.77³C is measured in the lower branch, Figure 8. The total uptake of catalyst pellet is 19.5 mg at point O and beyond this, 0.98 mg of condensed liquid is evaporated along the branch OA, as shown in Figure 9. The fractional liquid filling is reduced to 0.767 in the lower branch, Figure 10. The phase transition from lower to upper branch reaction rates is followed by the evaporation of 13.35 mg of condensed phase, shown in Figure 9. This is accompanied by 3.67³C temperature rise and the fractional liquid filling drops to 0.194. The effect of surrounding temperature on the extent of partial internal filling of catalyst pellet is clearly observed by comparing the extent of catalyst internal wetting at the

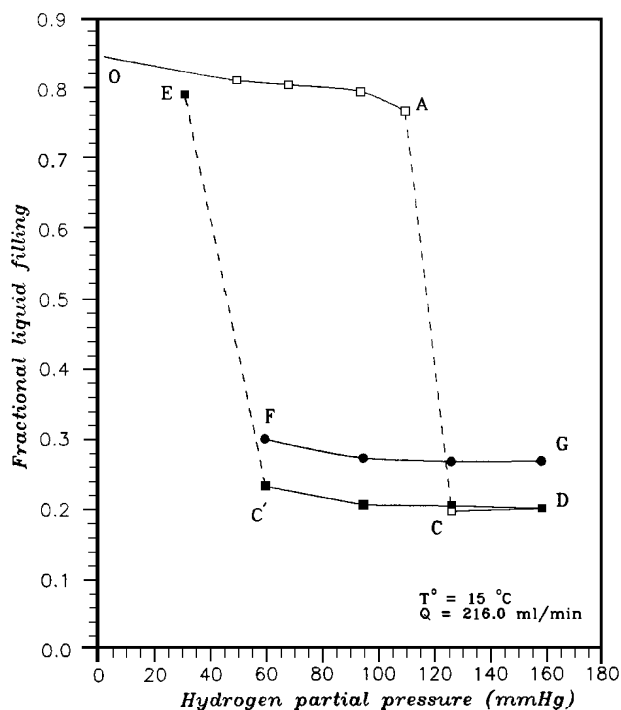


Figure 10. Variation of catalyst pellet fractional wetting with hydrogen partial pressure.

surrounding temperatures of 22 and 15³C.

The branch FG in Figure 7 corresponds to the observed reaction rates which starts with initially gas prefilled catalyst pores where condensation occurs during the course of reaction. The extent of catalyst fractional liquid filling in branch FG is different from the upper and lower branch reaction rates of catalyst pellet, Figure 10. This indicates that the state of catalyst pellet depends on its extent of internal wetting which is turn depends to its past history of states.

Table 2 summarizes the weight change, open pore volume and fractional liquid filling in TGA experimental runs. The open pore volume of catalyst pellet is calculated from the amount of evaporated condensed liquid along the branches OA and CD. Table 2 shows that about 0.023 ml/g if catalyst pore volume is open to gas transfer of species at branch OA.

Phase transition from predominantly liquid to predominantly gas filled pores occurs with

TABLE 2. Comparison of Fractional Liquid Filling of Pellet at Different Branches from TGA Experimental Results.

Q ml/min	T ³ °C	P _{H2} mm Hg		W _L mg Branch		V _P ml/g cat Branch		î _l ^T	
		A	C	OA	AC	OA	AC	A	C
216.0	15.0	110.5	126.3	1.61	13.35	0.026	0.223	0.767	0.194
216.0	22.0	107.2	122.5	1.20	16.24	0.020	0.272	0.795	0.077

T³: Bulk Temperature; Q: Flow Rate; P_{H2}: Hydrogen Partial Pressure; W_L: Weight of Evaporated Condensed Phase; V_P: Volume of Open Pores; î_l^T: Fractional Liquid Filling Calculated from TGA Results.

evaporation of condensed liquid from finer pores of catalyst pellet in which approximately 0.22 and 0.27 ml/gm pore volume of catalyst pellet is open to gas phase transfer of species at surrounding temperatures of 15 and 22°C respectively.

An additional experiment was carried out at the bulk temperature of 15°C and flow rate of 216.0 ml/min in order to confirm that the catalyst pellet is not deactivated while exhibiting the reaction rate corresponding to branch FG. The experimental run was directly started with the gas prefilled pores of catalyst pellet. For this purpose, the catalyst pellet was reduced in a small flow rate of hydrogen gas at the temperature of 200°C for about 8 hours prior to the experimental run. Figure 11 shows the results of this experimental run and also compares the observed reaction rates with symbol of (ú) corresponding to gas prefilled pores of catalyst pellet with the observed reaction rates with the symbol of (o). A good agreement is seen between the observed reaction rates of the confirmation test and

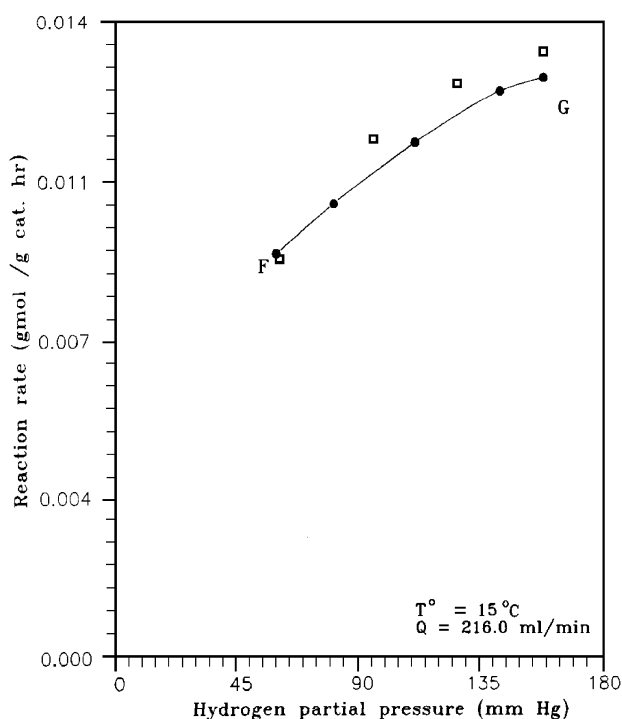


Figure 11. Comparison of reaction rate of fresh gas prefilled catalyst pellet with middle branch reaction rate of figure 7.

experimental results of Figure 7.

DISCUSSION

The experimental observations show that the catalyst pellet acquires different degrees of internal wetting at branch FG as compared to lower (OA) and upper branch (CD). This shows that the fractional liquid filling of pellet in branch FG is different from that of lower and upper branches and hence, the state of catalyst pellet. Therefore, the multiple steadystates of the internally wetted catalyst pellet is associated with a different degree of internal wetting and consequently different reaction rates are exhibited by catalyst pellet at the same hydrogen partial pressure value.

The fractional liquid filling of catalyst pellet can also be estimated from the Kelving and Cohan equations (1) and (2) and pellet surface temperature. As it is seen from the Kelvin

equation, a small uncertainty in the temperature of pellet has a disproportionately large effect on the estimated pore radius r_m . This may lead to a large magnitude of error in estimating the fractional wetting of pellet. In TGA experiments, the accurate measurement of pellet surface temperature was not possible due to limitation in the experimental set up. The TGA experiments confirm that the phase transition from predominantly liquid to predominantly vapor filled pores occurs during the exothermic reaction giving rise to a different degree of fractional wetting inside the pellet. The presence of mobile phases and the stationary phase (catalyst pellet) brings out the phase transition and reaction rate multiplicity.

CONCLUSIONS

The phenomenon of capillary condensation is experimentally investigated in this work. The experimental design permitted the direct measurement of the partial internal wetting in the catalyst pellet during the hydrogenation of cyclohexane over Pd catalyst pellet. Evaporation of condensed phase from pre-condensed catalyst pellet pores is a result of the heat liberated from exothermic reaction.

The condensed phase evaporation is confined to the macropores of catalyst pellet at lower branch reaction rate and it is extended over different hydrogen partial pressure during the course of reaction depending on reaction condition. The phase transition from lower to upper branch reaction rate is associated with the sharp temperature rise in catalyst pellet. A significant fraction of micropores volume is open at the upper branch reaction rate. The TGA results show that the gas prefilled catalyst pellet exhibits different degrees of internal wetting as compared to the state of catalyst

pellet at lower and upper branches.

The TGA results indicate that the reaction rate multiplicity is associated with different degrees of pellet internal wetting. The partially internally wetted catalyst can have any degree of internal wetting and hence exhibits reaction rate hysteresis between lower and upper branches. In calculating the fractional wetting of catalyst pellet from Kelvin and Cohan equations, the practical applicability of capillary condensation in the porous media must be taken into the consideration.

REFERENCES

1. Hanika, J., Sporka, K., Ruzicka, V. and Hrstka, J., "Measurement of Axial Temperature Profiles in an Adiabatic Trickle Bed Reactor," *Chem. Eng. J.*, 12, (1976), 193-197.
2. Sedricks, W., and Kenney, C. N., "Partial Wetting in Trickle-bed Reactor: The Reduction of Crotonaldehyde over a Palladium Catalyst", *Chem. Eng. Sci.*, 28, (1973), 559-568.
3. Miils, P. L. and Dudukovic, M. P., "Application of the Method of Weighted Residuals to Mixed Boundary Value Problems: Dual Series Relation", *Chem. Eng. Sci.*, 35, (1980), 1557-1567.
4. Sakornwimon, W. and Sylvester, N. D., "Effectiveness Factors for Partially Wetted Catalysts in Trickle-Bed Reactors", *Ind. Eng. Chem. Process Des. Dev.*, 21, (1982), 16-25.
5. Hessari, F. A and Bhatia, S. K., "Reaction Rate Hysteresis in a Single Partially Internally Wetted Catalyst Pellet: Experiment and Modeling", *Chem. Eng. Sci.*, 51, (1996), 1241-1256.
6. Jagusta, D. N. and Bhatia, S. K., "Partial Internal Wetting of Catalyst Particles: Hysteresis effects", *AIChE. J.*, 37, (1991), 650-660.
7. Kim, Y. and Kim, Y. G., "An Experimental Study of Multiple Steady States in a Porous Catalyst Due to Phase Transition", *J. Chem. Eng. Japan*, 14 (1981), 311-317.
8. Cohan, L. H., "Sorption Hysteresis and Vapor Pressure of Concave Surface", *J. Am. Chem. Soc.*, 60, (1938), 433-439.