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Experimental study of vaporization effect on steady state and dynamic behavior of catalytic pellets

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Abstract

The impact of the combined evaporation of the liquid phase and reaction on single catalyst pellet performance has been studied experimentally. The exothermic, catalyzed hydrogenation of α-methylstyrene (AMS) to cumene has been employed as a model reaction. Steady state and dynamic experiments have been performed in a single catalytic pellet reactor using five catalytic pellets of different porous structures, thermal conductivity, apparent catalytic activity and distribution of catalyst in the pellet. Gas-phase temperature, concentration of AMS in the gas phase and the liquid flow rates have been varied. The measured center and surface temperatures of each pellet reveal the existence of two significantly different steady states in the range of liquid flow rate. The range of the liquid flow rate over which the two steady states were observed, the pellet temperature and the pellet dynamics depend strongly on the amount of AMS vapor in the gas phase and the catalyst properties. The obtained experimental data are helpful to elucidate the mechanism of hot-spot formation and runaway in multiphase fixed-bed reactors.

Keywords: α-Methylstyrene; Cumene; Vaporization; Exothermic reaction; Catalyst; Pellet; Temperature

1. Introduction

Previous studies of trickle-bed reactors (TBRs) have mainly focused on operation under conditions where liquid volatility does not play a role. Porous catalyst pellets have been considered as being internally liquid filled even if they were only partially covered by liquid. However, several studies have demonstrated that vaporization of the liquid phase driven by the heat generated by exothermic reaction may have strong influence on the reactor behavior [1–5]. Watson and Harold [3] and Khadilkar et al. [5] presented reviews of these studies.

Vaporization with exothermic reaction has been shown to be much faster than vaporization without reaction. In particular, in their study of cyclohexene hydrogenation, Watson and Harold [3] found that the maximum vaporization rate with reaction is almost 500% higher than the corresponding maximum value without reaction. The increased vaporization rate may lead to a partially wetted and filled catalyst, within which both gas- and liquid-phase reactions occur, and to a completely dry pellet, within which only a gas-phase catalytic reaction occurs. External and internal drying of the catalyst inevitably leads to a change of the apparent reaction rate which in its turn influences the vaporization rate. Such an interplay between the exothermic reaction and phase transition processes can result in several steady states of the

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catalytic pellet with different fractions of dry external and internal surfaces.

Because of the more rapid mass transport and less efficient heat removal associated with a gaseous system, the overall rate of reaction in a partially or completely dry catalyst can be significantly higher than that of a completely wetted catalyst. In particular, Watson and Harold [4] observed an increase of a factor of up to 20 in cyclohexene hydrogenation rate for the same bulk conditions if dewetting is induced within the catalyst pores. This situation is problematic because of the increased potential for hot-spot formation or even a reactor runaway, see [1,3,6,7]. Several studies reveal that zones may exist within the reactor in which the local temperatures exceeds the boiling point of the less-volatile component, even though the feed temperature is well below this level, see [3].

Although there is an obvious progress in understanding of the role of phase transition processes in TBR, experimental data are available for only a restricted range of operating conditions and systems. Because of the industrial significance of hot-spot formation and runaway phenomena, the phase transition processes clearly demand further study.

The objective of the present study is to experimentally examine the combined effect of exothermic chemical reaction and phase transition on steady state and dynamic behavior of catalytic pellets. This is accomplished by carrying out a multiphase reaction in a single-pellet reactor. In contrast to similar previous experimental studies [3,4,8] attention has been paid to the influence of the following factors on catalyst behavior:

- liquid flow rate;
- fraction of the volatile liquid reactant present in the gas phase;
- gas temperature;
- properties of the catalytic pellets such as distribution of the catalytically active material in the pellets, apparent catalytic activity, porous structure and thermal conductivity.

2. Experimental setup and procedure

The experiments have been carried out in a single-pellet reactor similar to that employed in earlier studies. In contrast to the reactors used by Funk et al. [8] and Watson and Harold [3,4] our reactor was positioned horizontally and equipped with the specially developed gas saturator for presaturation of the gas phase entering the reactor with the vapors of liquid reagents. Different fractions of volatile reagent in the gas phase entering the reactor could be obtained by heating the liquid in the saturator.

The cylindrical reaction vessel, 15 mm internal diameter, was made of Pyrex glass and was surrounded by an annular glass air jacket to provide for an isothermal environment. A cylindrical catalytic pellet was placed in the middle of reactor in a vertical position. The liquid reagent was fed to the top of the catalytic pellet through a stainless tube with a diameter of 1 mm provided with a glass capillary at its end of a internal diameter of 0.2 mm. The small tube diameter and its length inside the reactor insured the liquid feed temperature to be equal to the bulk temperature. A scheme of the central part of the reactor is presented in Fig. 1.

Two thermocouples, 0.2 mm diameter, were carefully inserted onto the pellet. One thermocouple measured the temperature in the center of the particle (T_1), and the other one the temperature near the surface at a distance of 0.2–0.5 mm below the top (T_2). The thermocouples were sufficiently rigid to hold the pellets in a fixed position. The gas temperature (T_0) was measured with a moveable thermocouple, which allows for a temperature measurement at any point in the reactor (Fig. 1). The experimental setup included also the air heaters, the gas and liquid supplying systems and the control and monitoring devices. The

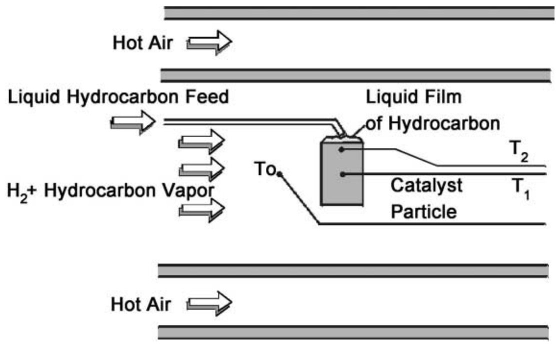

Fig. 1. Scheme of temperature measurements in single-pellet reactor.

Table 1
Properties of catalyst pellets

Pellet No.	Catalyst/support	Diameter × height (mm)	Total pore volume (cm^3/g)	Specific surface (m^2/g)	Pore data		Active component distribution
					Radius (Å)	Volume (cm^3/g)	
1	15% Pt/γ-Al_2O_3	4.8 × 5.7	0.65	206	40–1000 >1000	0.45 0.20	Uniform
2	15% Pt/γ-Al_2O_3	5.2 × 6.6	0.65	206	40–1000 >1000	0.45 0.20	Egg-shell
3	15% Pt/γ-Al_2O_3	5.2 × 6.6	0.65	206	40–1000 >1000	0.45 0.20	Egg-yolk
4	3.5% Pd/Ti–Al[a]	4.8 × 6.5	0.21	9	$>10^5$ 10^3–10^5 $<10^3$	0.10 0.09 0.02	Uniform
5	0.5% Pd/Sibunit[b]	4.8 × 4.8	0.35	300	200–300 40–70	0.20 0.15	Uniform

[a] Ti: 62.5 wt.%, Al: 37.5 wt.%.

[b] Porous carbon support.

exothermic hydrogenation of α-methylstyrene (AMS) to cumene has been utilized as a model reaction.

Steady state and dynamic experiments were performed using a gas phase containing hydrogen and AMS vapor. The fraction of AMS vapor in gas phase varied over the entire permissible range in order to elucidate the influence of the vapor–liquid equilibrium. The presaturated hydrogen gas was obtained in the saturator at a temperature slightly higher than that in the reactor. The small excess of AMS vapor condensed on the reactor wall.

All experiments were performed at atmospheric pressure and a constant hydrogen flow rate of 18.5 cm^3/s. In contrast to the previous studies of the AMS hydrogenation, the experiments were conducted at higher gas temperatures of 80–136°C. The liquid-phase flow rate varied from 0 to 2.5×10^{-3} g/s. During the dynamic experiments the liquid flow rate changed, whereas the other operating parameters have been kept the same.

The measured center and surface temperatures of the pellet characterize the thermal effects of exothermic reaction and endothermic evaporation, and informed us of a reaction rate multiplicity, internal filling of the pellet with liquid, and phase change inside the pellet. The degree of external liquid coverage was estimated by visual inspection through the glass reactor vessel during the experiment.

Five catalytic pellets of different porous structure, apparent catalytic activity, distribution of catalyst in the pellet and thermal conductivity were used in this study. Some of their properties are given in Table 1. In the pellets with the egg-shell catalyst distribution, the catalytic materials were deposited in an external layer of only 0.7 mm. On the contrary, an external layer of only 0.7 mm was not impregnated with the catalytic materials in the pellet with egg-yolk catalyst distribution.

3. Experimental results and discussion

3.1. Experiments with presaturated hydrogen

Fig. 2 shows the impact of the liquid flow rate and properties of the pellets on the center temperature (T_1). The temperature near the surface of the pellet (T_2) exhibited a similar behavior. We observe the existence of two steady states for each catalyst.

If the catalysts were in the upper steady state with liquid flow rates, which did not exceed certain critical values, the catalyst temperatures gradually decreased with the liquid supply. The slow decrease of the temperatures along the upper branches can be explained by the heat consumed for the heating and evaporation of the increasing amount of the liquid feed. Since the

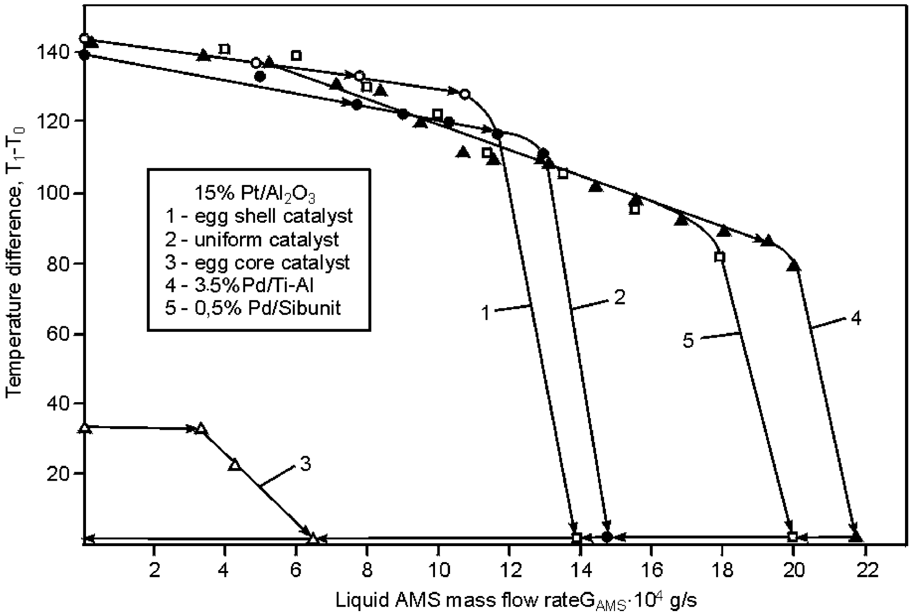

Fig. 2. The impact of the AMS liquid mass flow rate and pellet properties on the steady state of the catalyst for H_2 saturated with AMS. Gas temperature: 125°C, vapor AMS saturated molar fraction: 0.3.

gas feed temperature T_0 was above 80°C, the center and surface temperatures of the pellets 1, 2, 4 and 5 in the upper branches are considerably higher than the boiling point of AMS, which is 165.4°C. Also no liquid could be observed at the lower and side surfaces of the pellets. This is an indication that the liquid AMS evaporated completely.

When the liquid feed rates exceed the critical values, the temperature of the catalysts abruptly decreased to a temperature practically equal to the gas temperature. The steady state of the catalyst particle changed from a vapor-filled state to the completely liquid-filled state. In the low steady-state liquid droplets hanging on the bottom of the pellet and falling down can be observed. Further, increase or decrease of the liquid flow rate does not influence the temperatures of the catalysts. The catalysts remained in an internally fully wetted condition. A decrease of liquid supply even up to zero ($G_{\mathrm{AMS}} = 0$) also does not result in the temperature change for at least 30 min. This means that the pores of the pellets remained filled with liquid even without liquid feed provided the gas phase fully saturated with AMS. This result disagrees with the observations in [3], where it does not detect the low-rate steady state for the liquid-filled pellet exposed to hydrogen saturated with cyclohexene at room temperature and normal pressure.

The obtained data show that pellets with a uniform or egg-shell type distribution of the active component exhibit practically the same behavior. The temperature difference $T_1 - T_0$ in the upper branches was about 80–140°C for all four pellets. For the egg-yolk type catalyst, the particle–gas temperature difference $T_1 - T_0$ in the upper branch and the critical liquid flow rate are much lower than for the other pellets. This can be attributed to mass transfer resistance in the catalytically inactive layer of the egg-yolk type catalyst.

The critical liquid flow rates for pellets 4 and 5 were found to be as much as 1.5 of that for 15% Pt/Al_2O_3 catalysts. We assume that the higher thermal conductivity of pellets 4 and 5 (1.0–1.5 W/(m K)) compared to the low thermal conductivity of pellets 1–3 (0.2–0.3 W/(m K)) (γ-Al_2O_3-supported catalyst) is responsible for the higher critical liquid flow rates.

The low-temperature steady state is rather sensitive to a deviation from the vapor–liquid equilibrium. The sensitivity increases with decreasing liquid flow rates. Transition of the reaction from the lower to the upper branch occurs for $G_{\mathrm{AMS}} = 0$, if the gas composition was slightly disturbed from the phase equilibrium

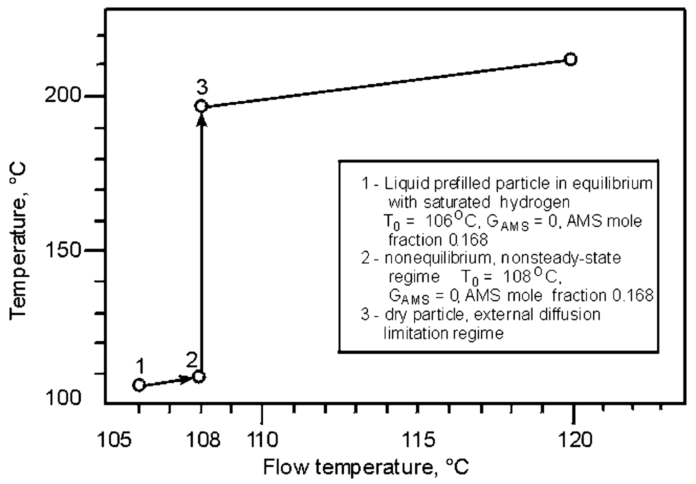

Fig. 3. Influence of the bulk gas temperature increase on the pellet temperature. Catalyst — 15% Al_2O_3 with uniform Pt distribution; $G_{AMS} = 0$.

state. Fig. 3 illustrates this phenomenon for the case of no liquid feed to the pellet. In this experiment, the low-rate steady state being the lower branch in Fig. 2, was attained at a gas temperature of 106°C and for a gas phase consisting of hydrogen and saturated AMS vapor (point 1 in Fig. 3). Then the gas temperature was increased to 108°C without changing the gas-phase composition, so there is no more a phase equilibrium in point 2 in Fig. 3. The mentioned temperature change corresponds to a change of the AMS vapor mole fraction from 0.168 to 0.182. This 2°C change of the gas temperature resulted in a transition of the reaction to a gas-phase within: this few minutes results in an increase of the pellet temperature from 108

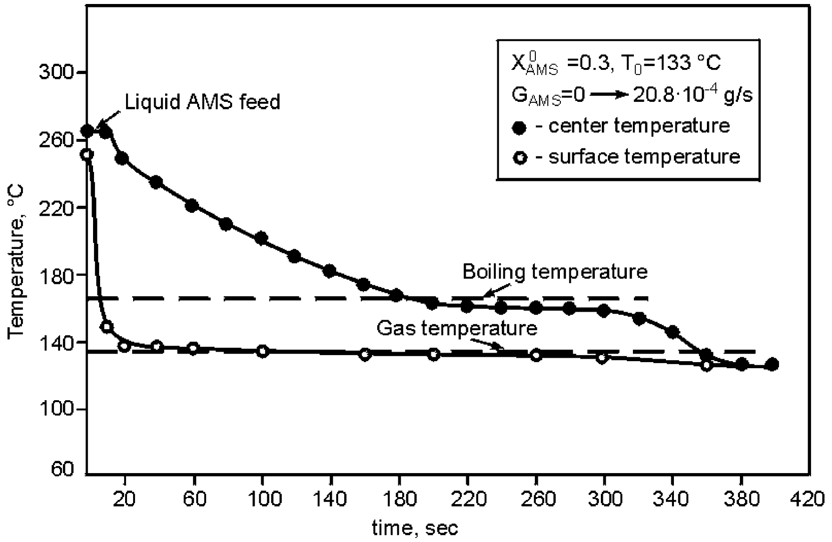

Fig. 4. Time dependence of the pellet temperatures during a transition from vapor–gas to liquid phase. Catalyst — 15% Pt/Al_2O_3 with uniform active component distribution.

to 200°C. Resulting temperature rise 92°C is lower than in Fig. 2 (140°C), because the gas temperature and hence saturated vapor concentration is lower.

The filling dynamics of catalyst pellet supplied with liquid and then blowing of partially saturated hydrogen is presented in Fig. 4. The time of transient regime in this case is determined by the ratio between the pellet impregnation rate and the liquid vaporization rate. Due to the contact with liquid, the temperature of the wetted surface achieves the gas temperature in 20 s. The temperature in the pellet center changes more slowly and attains the AMS boiling point in 200 s, while the whole transient mode lasts 380 s. As the boiling point has been attained, the pellet temperature remains almost the same for ∼100 s that indicates the presence of intensive liquid evaporation within the pellet porous structure. The temperature of the new steady-state regime is lower than the gas temperature by ∼10°C.

3.2. Experiments with pure hydrogen

The experiments with pure hydrogen were performed in a similar way as the experiments with presaturated hydrogen. Fig. 5 shows center temperatures of pellets in the steady state for two pellets at different gas temperatures. The arrows in Fig. 5 indicate the succession in which the steady states were attained.

As in the case with saturated hydrogen, two steady states exist for certain ranges of the liquid flow rates. A similar multiplicity phenomenon was obtained in [1]. Comparison of Figs. 2 and 5 shows that the steady-state behavior of the pellets changed considerably when pure hydrogen feed is replaced by the presaturated hydrogen.

The temperatures of the pellets are 20–30°C higher than the gas temperature and significantly lower than the temperatures of the same pellets in the experiments with the presaturated hydrogen (Fig. 2). This difference in temperatures could be expected because of the evaporation of AMS from the pellets: there was no AMS in the gas feed entering the reactor and hydrogen carries away the evaporated AMS. It must be noted that the temperature of the pellets in the upper branches rises with the increase of the liquid flow rate. This can be attributed to higher concentrations of the evaporated AMS in the gas phase.

According to visual observations the pellets were almost completely wetted at the low-temperature steady states. Their temperatures were 20–30°C lower than the gas temperature. In contrast with the temperatures of the same pellets exposed to the presaturated

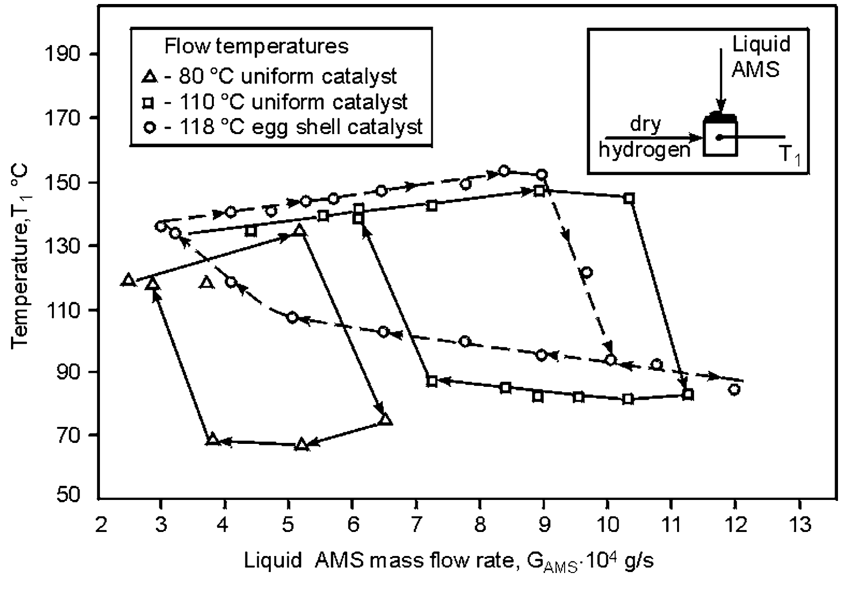

Fig. 5. Hysteresis phenomena on the catalyst pellet. Catalyst — 15% Pt/Al_2O_3 with uniform and egg-shell active component distribution.

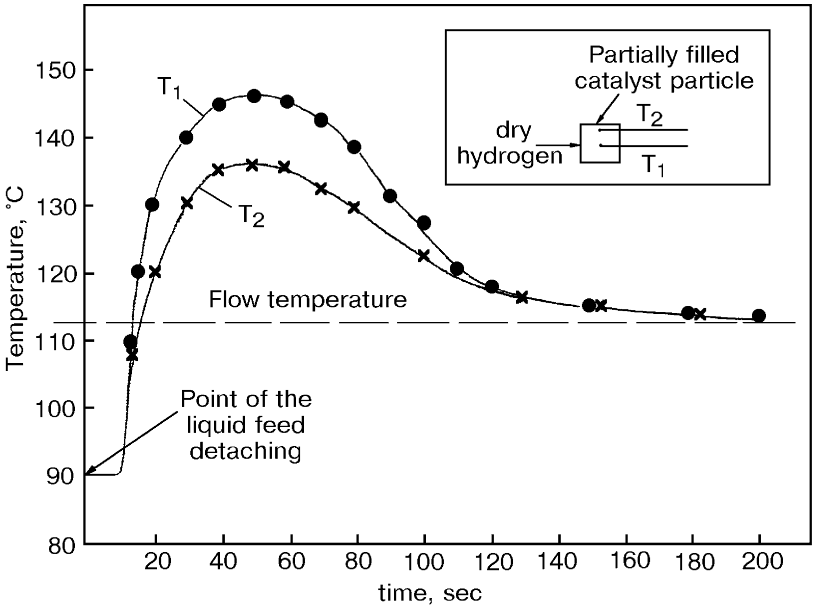

Fig. 6. Dynamics of the pellet drying.

hydrogen (Fig. 2). These low temperatures of the pellets can be explained by the intensive evaporation of AMS in pure hydrogen, due to the significant deviation from the vapor–liquid equilibrium.

Fig. 5 shows that the critical liquid flow rates at which transitions from the upper to the lower branch occurred are lower than in the same experiments with the saturated hydrogen; further they strongly depend on the gas temperature.

If the reaction occurred in the low-rate steady state and the liquid feed rate was reduced, the reaction continued along the fully wetted, low-rate branch until it reached the ignition point, where it abruptly shifted to the dry, high-rate branch. This represents the initiation point of intra-catalyst drying. Both the ignition point and the temperature in the fully wetted state depend on the catalyst properties (Fig. 5). No such dependence was observed in the experiments with presaturated hydrogen (Fig. 2).

Variations of the temperatures of the pellets exposed to pure hydrogen after stopping the liquid feed are shown in Fig. 6. This experiment mimics a sudden loss of liquid flow in the reactor. After a short period, required for increasing of the dry area, the catalytic pellet changed from almost completely wetted to a vapor-filled state and its temperature increased from 90 to 135–145°C. After passing a maximum the temperature decreased, since the liquid content in the particle decreases and so did the evaporation rate of AMS. Similar pellet behavior was observed by Watson and Harold in [3] who found that a pellet prefilled with cyclohexene and then exposed to pure hydrogen exhibited a temperature rise of nearly 100°C and dried out rapidly in few minutes of time.

The observed intra-particle temperature gradient was less pronounced than in the dynamic experiments with the presaturated hydrogen (Fig. 4). Nevertheless it was sufficiently large to assume the existence under the transient conditions of a reaction–evaporation front inside the pellet.

We observed the ignition and extinction phenomena at liquid flow rates of the order of 10^{-3} g/s. These flow rates correspond to the superficial liquid velocities of about 0.03 mm/s, which are much lower than the superficial liquid velocities of 3–4 mm/s as used in industrial TBRs. Since the industrial reactors operate at high pressures, the liquid-phase reaction rates are much higher than in our experiments, we expect that multiplicity of steady states under industrial conditions may occur at superficial liquid velocities significantly higher than 0.03 mm/s. On the other hand, local superficial velocities of about 0.03 mm/s are not unrealistic in industrial reactors because of the liquid maldistribution and the influence of reaction on hydrodynamics and vaporization. The effect of liquid flow rate on pellet behavior corroborates previous observations that liquid maldistribution can result in hot-spot formation in TBRs.

4. Conclusions

The performed experiments for the hydrogenation of AMS to cumene demonstrate on the single-pellet level the significance of phase transition processes during an exothermic multiphase catalytic reactions.

Two stable steady states for the catalytic pellet in a certain range of liquid flow rates can be obtained due to the vaporization of the liquid both flowing over the external catalyst surface as well as that filling the pore structure. The two steady states at the same ambient conditions differ in their temperatures and internal filling with liquid. The temperatures of the pellets, their external and internal wetting and the critical liquid flow rates at which ignition and extinction take place, depend strongly on the fraction of AMS vapor in the gas phase, gas temperature and properties of the pellets. The apparent catalytic activity, thermal conductivity of the pellet, its porous structure and distribution of the catalyst in the pellet are also important factors which can influence the pellet behavior.

The most dangerous situation in a TBR occurs when the gas phase consists of a mixture of hydrogen and saturated AMS vapor: in this case the low-temperature state is rather sensitive towards the operating conditions especially at low liquid flow rates, while the temperature of the pellets after ignition increases as much as 140°C and significantly may exceed the liquid boiling point of the liquid.

The data obtained confirm previous observations in [1] that reaction itself has an influence on the hydrodynamic behavior of a trickle bed, due to evaporation and external wetting. The steady state and dynamic single-pellet experiments help to identify situations in which hot spots may form and provide us with the data necessary for testing of the available and new models of TBRs.

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