ELSEVIER

Catalysis Today 48 (1999) 301–306

CATALYSIS TODAY

Trickle bed reactor diluted with fine particles and coiled tubular flow-type reactor for kinetic measurements without external effects

Hiroshi Yamada, Takafumi Naruse, Shigeo Goto*

Department of Chemical Engineering, Nagoya University, Furo-cho Chikusa-ku, Nagoya 464-8603, Japan

Abstract

Gas and liquid velocities in laboratory scale trickle bed reactors are one or two orders of magnitude lower than those in commercial reactors. Then, the kinetic data may include the external effects. This shortcoming of laboratory scale trickle bed reactor can be resolved by diluting the catalyst bed with fine inert particles. The catalyst bed dilution increases dynamic liquid holdup, pressure drop, gas–liquid mass transfer coefficient. Hydrogenation of 2-phenylpropene on Pd/Al_2O_3 was performed with the trickle bed reactor diluted with fine inert particles and the coiled tubular flow-type reactor to compare the kinetics with that of the basket type batch reactor. The trickle bed reactor diluted with fine inert particles is suitable to obtain the reaction rate without external effects even if the liquid velocity is low. The coiled tubular flow-type reactor should be used at high gas velocities. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Hydrogenation; Trickle bed reactor; Coiled tubular flow-type reactor

1. Introduction

The laboratory three-phase reactors to obtain kinetic information for the design of commercial reactors, as well as for the evaluation of newly developed catalysts, should be designed to provide the kinetic data without any external effects such as heat, mass transfer resistances and axial dispersion.

Batch-type reactors can be effectively used to measure the kinetics with stable catalytic activity without the external effects, because a number of kinetic data can be efficiently obtained in a shorter span of experimental time with a batch-type reactor than with a flow-type reactor. Novel stirred type batch reactors with the exact starting time of reaction in batchwise experiments even at high pressure and temperature have been developed by Ishigaki and Goto [1,2], that is, an improved basket-type batch reactor for pelletized catalysts [1] and a reactant injection type batch reactor for powdered catalysts [2].

When the activity of catalyst gradually changes, the processes of reaction and the catalyst deactivation cannot be decoupled in batch-wise experiments. In such a case, trickle bed flow-type reactors are widely used for the kinetic measurements.

Gas and liquid velocities in laboratory scale trickle bed reactors are usually one or two orders of magnitude lower than those in commercial reactors due to the restriction of the height of reactor, which results in the kinetic data incorporating the external effects. The shortcoming of laboratory trickle bed reactor can be resolved by diluting the catalyst bed with fine inert particles [3–6]. The dilution reduces axial dispersion

---

*Corresponding author. Tel.: +81-52-789-3261; fax: +81-52-789-3261; e-mail: goto@nuce.nagoya-u.ac.jp

PII: S0920-5861(98)00385-X

substantially to the extent where plug-flow can be established and much higher liquid hold-up improves the wetting contact efficiency at lower velocities of gas and liquid. In this method, the uniformity of dilution may affect the residence time distribution of liquid in the bed. Hence, the dilution should be carefully carried out to obtain reproducible data.

Alternatively, a coiled tubular flow-type reactor has been developed to obtain the kinetics, at high gas and liquid velocities with long liquid contact time as in commercial reactors [7]. A narrow and long tube was helically coiled to reduce the height of reactor.

In this paper, experiments were carried to evaluate the trickle bed reactor diluted with fine particles and the tubular flow-type reactor for kinetics determining apparatus. The effects of the catalyst bed dilution were quantitatively evaluated by measuring dynamic holdup, pressure drop, gas–liquid mass transfer coefficient and kinetics of hydrogenation of 2-phenylpropene (α-methylstyrene) on Pd/Al_2O_3. The reaction was also performed in the coiled tubular flow-type reactor to compare the kinetics in the diluted catalyst bed.

2. Hydrodynamic studies on trickle bed reactor with and without fine particles

2.1. Apparatus

A trickle bed reactor (2.7 cm inner diameter and 32 cm height) packed with coarse glass beads (5.2 mm in diameter) was used for measurements of liquid holdup, pressure drop, gas–liquid mass transfer coefficient and reaction rate of hydrogenation of 2-phenylpropene. Fig. 1 shows the experimental apparatus. The liquid entered the top of the bed through a distributor containing 20 capillary tubes (0.5 mm inner diameter). The experiments were done under atmospheric pressure. Fine glass beads (0.5 mm diameter) were used as fine particles.

The following technique recommended by Al-Dahhan et al. [3,4] was adopted for the diluted bed. At first, a portion of coarse particles was loaded to the reactor with vibrating. Then, a portion of fine particles was gently loaded with vibrating until the fine particles appeared at the top layer of coarse particles. This procedure was repeated until specified amounts. The volume ratio of coarse glass beads to fines was 3. Void fractions of bed were measured by using a measuring cylinder. The values of void fraction were 0.40 and 0.21 for the packed beds without and with fines, respectively. Therefore, the void fraction in the diluted bed was about half of that in the undiluted bed. On the other hand, the void fraction in the fine bed packed with only fine glass beads was 0.39. Thus, the void fraction in uniform packing was independent of sizes.

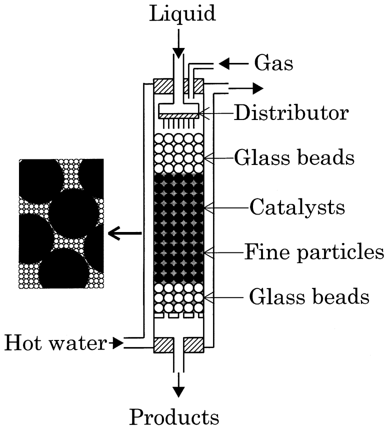

Fig. 1. Trickle bed reactor diluted with fine particles.

2.2. Dynamic liquid holdup

Distilled water and nitrogen gas were used as liquid and gas, respectively. For dynamic liquid holdup measurements, the inlet and outlet valves were simultaneously closed after steady state conditions were achieved. Then, the drain volume of liquid was measured. Experiments were carried at room temperature.

Fig. 2 shows the effect of liquid velocity on the dynamic liquid holdup. The dynamic liquid holdup for the diluted bed packed with the mixture of two sizes of glass beads was the middle of two holdups for the fine bed packed with only fine glass beads and the undiluted bed packed with only coarse glass beads.

The correlation of Otake and Okada [8] can be applied only for the undiluted bed and has a good agreement with the experimental data.

2.3. Pressure drop

The pressure drop was measured by the manometer at the inlet of reactor. Fig. 3 shows the effect of liquid

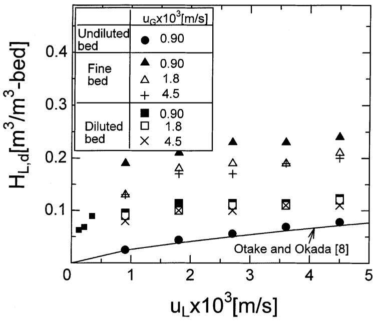

Fig. 2. Effect of gas and liquid velocities on dynamic liquid holdups.

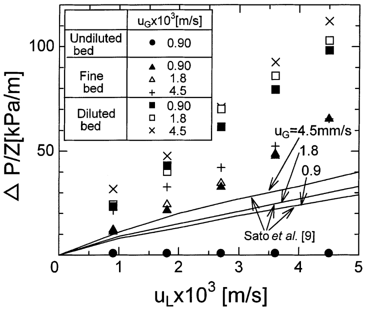

Fig. 3. Effect of gas and liquid velocities on pressure drop.

velocity on the pressure drop. The pressure drop for the undiluted bed is negligibly small. The pressure drop for the fine bed can be compared with the result estimated from the correlation of Sato et al. [9] which is about half of experimental data. The pressure drop for the diluted bed is the highest because the void fraction is half of the undiluted bed.

2.4. Gas–liquid mass transfer coefficient

The volumetric coefficients of mass transfer from gas to liquid were determined by the gassing-out method. At first, air was bubbled to saturate the distilled water in a feed tank which temperature was 303 K. Then, distilled water was introduced into reactor with nitrogen and the experimental run started. Distilled water was corrected at the outlet of reactor and the concentration of dissolved oxygen was measured by DO meter. The volumetric coefficient was calculated from the oxygen concentration. The end effects at the distributor and the bottom of the reactor were removed by the same method as that of Goto and Smith [10].

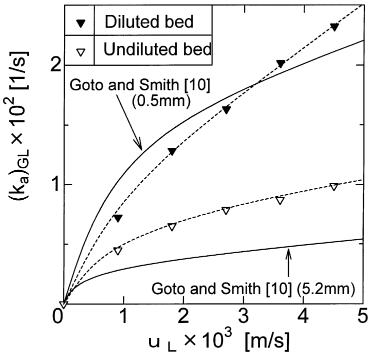

Fig. 4. Gas–liquid volumetric mass transfer coefficients.

Fig. 4 shows the effect of liquid velocity on the gas–liquid mass transfer coefficient. The volumetric coefficients for the diluted bed are higher by about two times than those in the undiluted bed.

Correlation of Goto and Smith [10] determined for three sizes (0.541, 2.91 and 4.13 mm) may be modified for two sizes (0.5 and 5.2 mm) on the assumption of inverse proportion with the size. The solid lines in Fig. 4 show the estimated results. The experimental values for the diluted bed are close to the line for the fine bed.

3. Kinetic studies on hydrogenation of 2-phenylpropene

3.1. Catalyst and reaction conditions

Hydrogenation of 2-phenylpropene (α-methylstyrene) to 2-phenylpropane (cumene) was chosen as a model reaction. 0.5 wt% Pd/Al_2O_3 with 3.7 mm diameter (manufactured by Engelhard) was used as a spherical catalyst. Pure 2-phenylpropene and hydrogen were introduced to the reactor as liquid and gas, respectively. The reaction temperature was 313 K and the pressure was atmospheric.

The products were analyzed by a gas chromatograph equipped with a column (PEG-20M 3 m, DOP 1 m) and TCD. The concentration of 2-phenylpropane was measured to determine the reaction rate.

3.2. Basket type batch reactor

A basket type batch reactor was used for pelletized catalysts (3.7 mm) to avoid the sedimentation. 3.4 g of catalyst was packed in two baskets and 2-phenylpropene of 1.6×10^{-4} m^3 was poured into the reactor. When the temperature reached 313 K, H_2 was introduced into the reactor, and then the reaction started.

Plots of the concentration of 2-phenylpropane and time could be drawn on the straight line. The reaction rate can be calculated from the slope of the straight line by the following:

$$R_A = \frac{V_B}{W_B}\frac{dC}{dt_B}. \qquad (1)$$

The reaction rates were determined by changing flow rates of hydrogen, rotating speeds and weights of catalyst in a basket type batch reactor.

As an example, Fig. 5 shows the effect of rotating speed of stirrer on the reaction rate. The observed reaction rate becomes constant over 300 rpm.

The reaction rate without external effects could be determined as 2.0×10^{-3} mol/(kg s) in this work.

It is well known that the reaction rate obeys the first order with respect to the concentration of H_2 in the liquid phase and the zeroth order with respect to 2-phenylpropene [11]. Therefore, the observed reaction rate constant could be calculated as 2.2×10^{-4} m^3/(kg s) from 2.0×10^{-3} mol/(kg s) divided by 9.10 mol/m^3 which was the saturated concentration of H_2 in the liquid phase at 313 K [11]. The intrinsic rate constant and the effective diffusivity for 0.5 wt% Pd/Al_2O_3 were reported as 1.2×10^{-3} m^3/(kg s) and 2.78×10^{-9} m^2/s, respectively (Table III in [11]). The effectiveness factor for 3.7 mm spherical catalyst used in [11] could be estimated as 0.02. The apparent rate constant (the product of the intrinsic rate constant and the effectiveness factor) was 2.4×10^{-4} m^3/(kg s) which was a little higher than that in this work.

3.3. Trickle bed reactor

Twenty gram of catalyst was packed into a trickle bed reactor (2.6 cm inner diameter and 45 cm height) with a jacket in which hot water was circulated at 313 K. α-Alumina (0.1 mm diameter) which was not active for this reaction was filled in a diluted bed by the recommended technique of Al-Dahhan et al. [3,4].

Fig. 6 shows reaction rates with time. The reaction rate of trickle bed can be calculated from the assumption of a differential reactor by the following:

$$R_A = \frac{V_F}{W_F}\frac{C_{exit}}{\tau}. \qquad (2)$$

The reaction rates at the steady state for the diluted bed are much higher than those for the undiluted bed.

Fig. 7 shows the effects of liquid velocity on the reaction rate. In the case of the diluted bed, the reaction rate is independent of the liquid velocity and is close to the rate without external effects obtained from the basket type batch reactor. On the other hand, in the case of undiluted trickle bed (downflow), the reaction rates for lower liquid velocities are unstable and smaller than the rate without external effects. It was revealed from observations that some pellets of catalyst were completely dried. Therefore, they might make no contributions to the reaction.

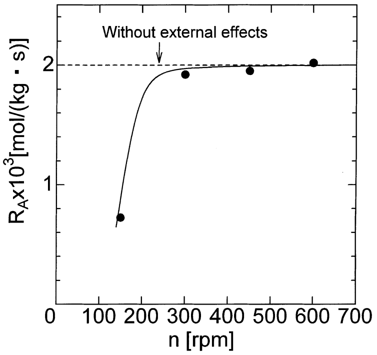

Fig. 5. Effect of rotating speed on reaction rate $u_G=3.2\times10^{-3}$ m/s.

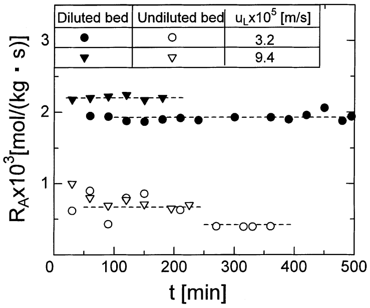

Fig. 6. Reaction rate versus time $u_G=3.2\times10^{-3}$ m/s.

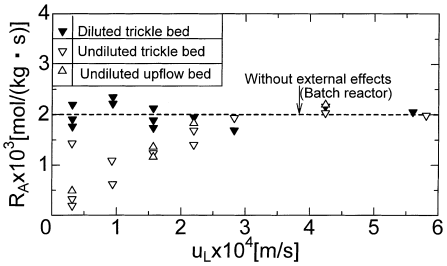

Fig. 7. Reaction rate versus liquid velocity u_G=3.2×10^{-3} m/s.

An undiluted upflow bed was used to check the effect of flow directions of gas and liquid. Although the upflow type is more stable, there are no big differences between downflow and upflow.

In the case of diluted bed, the liquid flow was homogeneous and stable as seen from the hydrodynamic studies. Even if the liquid velocity is low, the diluted bed is suitable to obtain the reaction rate without external effects.

3.4. Coiled tubular flow-type reactor

A coiled tubular flow-type reactor has been developed to obtain the kinetics, at high gas and liquid velocities with long liquid contact time as in commercial reactors [7].

Fig. 8 shows the apparatus. A straight glass tube (1.2 cm inner diameter, 5 m length) was helically coiled at about 5–10° tilt and in 12 cm diameter. The reactor was placed in a jacket to maintain the temperature at 313 K. Twenty gram of catalyst was packed into a coiled reactor. High velocities of gas and liquid can be easily attained with the coiled reactor at lower feed rates than with trickle bed reactors, due to smaller reactor diameter. Plug-flow and the absence of interphase mass and heat transfer resistances can be expected in the coiled reactor. The reaction rate was calculated by Eq. (2).

Liquid velocity was varied from 1.3×10^{-4} to 1.3×10^{-3} m/s at gas velocity 1.5×10^{-2} m/s. In this range, the reaction rate was independent of the liquid velocity.

Fig. 9 shows the dependence of the reaction rate on gas velocity. The observed reaction rate increases with gas flow rate and approaches to the reaction rate without external effects which was obtained from the basket type batch reactor.

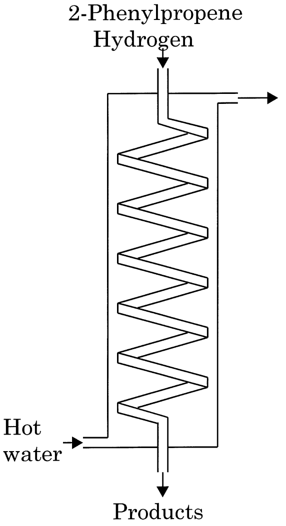

Fig. 8. Coiled tubular flow-type reactor.

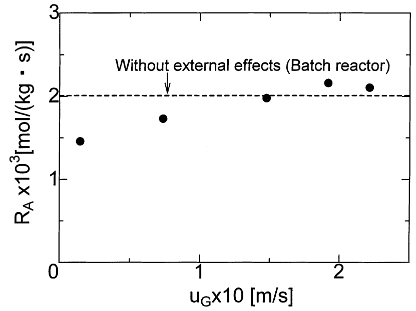

Fig. 9. Reaction rate versus gas velocity u_L=1.2×10^{-3} m/s.

Flow patterns of gas and liquid were observed by eyes. At lower gas velocities, gas flew in the upper part of tube and could not mix with liquid completely and then the reaction rate was lower. At higher gas velocities, gas and liquid were dispersed well and external effects of mass transfer could be negligible.

Therefore, higher gas velocities than 0.15 m/s may be required to obtain the reaction rate without external effects.

4. Conclusion

At first, the dynamic holdup, pressure drop and gas–liquid mass transfer coefficient were measured in three kinds of trickle bed, a diluted bed, an undiluted bed and a fine particles bed. Dilution of bed with fine particles increased liquid holdup, pressure drop and mass transfer rates.

Next, kinetics of hydrogenation of 2-phenylpropene on Pd/Al_2O_3 was investigated in a basket type batch reactor, a trickle bed reactor, an upflow reactor and a coiled tubular reactor. The diluted trickle bed reactor is suitable to obtain the reaction rate without external effects even if the liquid velocity is low. The coiled tubular flow-type reactor should be used at high gas velocities.

5. Nomenclature

C	liquid phase concentration of 2-phenylpropane (mol/m^3)
$H_{L,d}$	dynamic liquid holdup (m^3/m^3-bed)
$(ka)_{GL}$	volumetric mass transfer coefficient (1/s)
ΔP	pressure drop (Pa)
R_A	reaction rate (mol/(kg s))
t_B	reaction time for batch reactor (s)
u_G	superficial gas velocity (m/s)
u_L	superficial liquid velocity (m/s)
V_B	liquid volume in batch reactor (m^3)
V_F	volume of catalyst bed in flow-type reactor (m^3)
v_L	liquid volumetric flow rate (m^3/s)
W_B	catalyst loading in batch reactor (kg)
W_F	catalyst loading in flow-type reactor (kg)
Z	bed height (m)
τ	space–time in flow-type reactor ($=V_F/v_L$) (s)

References

[1] S. Ishigaki, S. Goto, J. Chem. Eng. Jpn. 27 (1994) 309.

[2] S. Ishigaki, S. Goto, J. Chem. Eng. Jpn. 30 (1997) 64.

[3] M.H. Al-Dahhan, Y. Wu, M.P. Dudukovic, Ind. Eng. Chem. Res. 34 (1995) 741.

[4] M.H. Al-Dahhan, M.P. Dudukovic, AIChE J. 42 (1996) 2594.

[5] J. van Klinken, R.H. van Dongen, Chem. Eng. Sci. 35 (1980) 59.

[6] Y. Wu, M.R. Khadilkar, M.H. Al-Dahhan, M.P. Dudukovic, Ind. Eng. Chem. Res. 35 (1996) 397.

[7] S. Ishigaki, S. Goto, J. Chem. Eng. Jpn. 28 (1995) 329.

[8] T. Otake, K. Okada, Kagaku Kogaku (Chem. Eng. Jpn.) 17 (1953) 176.

[9] Y. Sato, T. Hirose, F. Takahashi, M. Toda, J. Chem. Eng. Jpn. 6 (1973) 147.

[10] S. Goto, J.M. Smith, AIChE J. 21 (1975) 706.

[11] S. Morita, J.M. Smith, Ind. Eng. Chem. Fundam. 17 (1978) 113.