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The selective hydrogenation of butyne-1,4-diol by supported palladiums: a comparative study on slurry, fixed bed, and monolith downflow bubble column reactors

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Abstract

The present study was carried out to asses performance of a Pd-monolith downflow bubble column (DBC) reactor, and compare it with that of the slurry and the fixed bed DBC. The selective hydrogenation of butyne-1,4-diol to *cis*-2-butene-1,4-diol over palladium catalyst was chosen as a model reaction. In principle, the monolith DBC allowed the reaction to take place under kinetic control regime. Comparison with DBC employing 5% Pd/C powder and 1% Pd-on-Raschig ring catalysts revealed a better performance of the monolith DBC (1% Pd loading) with advantage of smaller reaction volume and intensified reaction rate. In the monolith DBC, improved hydrogen transport was possible, as the interface between bubbles and the channel wall was very thin, thus, the length of the diffusion path was very short. In addition, the interfacial surface area at both gas–liquid and liquid–solid interface in the monolith was also very high. The reaction kinetics was well represented by the Langmuir–Hinshelwood mechanism. As an alternative to conventional three-phase reactors, the monolith DBC was simple due to its inherent characteristic operation and no specially designed device.

Keywords: Palladium; Monolith; Structured catalyst; Bubble column; Fixed bed reactor; Hydrogenation

1. Introduction

Monolith structures are ceramic blocks of small parallel and straight channels. On the walls of the channel a thin layer of catalytic material is deposited, providing a reasonable external surface area and a short diffusional distance. In recent years, the monoliths have been suggested as one of valuable designs for solid-catalysed gas–liquid reactions. The design offers the potential for a fixed-bed reactor that inherently possesses a multi-step and multi product capability [1]. In comparison with the conventional type of catalytic reactors, the monolith reactor offers several advantages; low pressure drop due to open macro-structure, short gas diffusion path thus promoting mass transfer, high surface/volume ratio, and relative ease in scale-up.

The main issue in monolith reactor design is the demand for proper gas–liquid distribution that ensures well distribution of Taylor flow (Fig. 1) in the monolith. Between the bubble and the channel wall, a thin liquid film is found, through which gas is readily transferred to surface of the wall where catalytic material is deposited. This film tends to remain at the wall when the liquid plug flows. As the result, a circulation pattern occurs inside liquid plug, resulting in enhancement of gas transfer from the bubble caps to the wall [2]. For Taylor flow regime, it is expected that a closer approach to plug flow behaviour occurs due to sharp residence time distribution of gas and liquid, giving prospect for better selectivity towards the desired intermediate product in consecutive reactions [3].

Much research has been carried out in an attempt to find the best reactor configuration to optimise the novel features offered by the monolith. In a downflow bubble column (DBC) reactor, gas and liquid are introduced into the top section of the column simultaneously via an ejector or an orifice. As a result, a stable and closely packed bubble dispersion is formed in the column. When this kind of dispersion was applied to the monolith catalyst, flow

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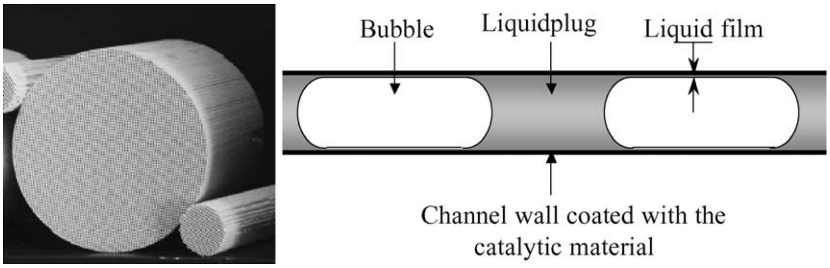

Fig. 1. Monoliths and illustration of Taylor flow in a monolith channel.

visualization by magnetic resonance imaging technique revealed well-distribution of Taylor flow in the monolith [4]. It is important since gas–liquid distribution has been great concerns in designing fixed bed reactors. Most reactors suffer bad phase distribution when scaling-up resulting in loss of their efficiency. Therefore, the monolith DBC shall gain attractiveness in solid catalysed three-phase reaction due to simplicity in design and operation.

The present paper reports on the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol evaluated in a monolith DBC, and compared with reaction performances observed in two conventional mode operation of DBC, i.e. slurry and fixed bed. 2-Butene-1,4-diol is an important intermediate due to its use in the production of several insecticides and pharmaceuticals (i.e. endosulfan and vitamin B6). Our previous work [5] has revealed the reaction network showing the desired product *cis*-2-butene-1,4-diol and the possible unwanted products including 1,4-butanediol, butyraldehyde, *cis*/*trans*-crotyl alcohol, and *n*-butanol due to further hydrogenation, hydrogenolysis and isomerization. The selectivity towards *cis*-2-butene-1,4-diol is a function of catalyst loading, temperature, solvent, base addition, metal additives, and support.

2. Experimental

2.1. Preparation of palladium on monolithic support

The cordierite monolith block pre-washcoated with α-alumina (Johnson Matthey & Co. Ltd., UK) (diameter = 9.3 cm, length = 15.24 cm) has 400 square channels/in.^{2} and void fraction of 41%. Palladium was impregnated at 1% (w/w) metal loading based on support weight. The catalyst precursor was sodium tetrachloropalladate (II) (Aldrich, UK). The impregnation was carried out by dip-coating method. The monolith was dipped partially in the Pd solution (6 g Pd salt in 750 ml deionised water) for 4 h and, it was reversed every hour. The solution entered the monolith channels by capillary action. To avoid channel plugging, excess solution in the channels was blown out gently. The wet monolith was then dried in an oven at 150 °C overnight. Finally, the dried monolith was calcined in air at 300 °C for 12 h. The Pd monolith was reduced in situ by wet method in hydrogen-saturated-water flow at room temperature. The reduction was completed when the monolith colour turn into black.

2.2. Experimental procedure

The experimental setup of the Pd-monolith DBC system is shown in Fig. 2. The reactor used was a 1.25 m length downflow bubble column made of QVF glass (Corning Glass) where a monolith block was placed inside the column, 85 cm from the reactor inlet. There was annular space between the monolith (diameter 93 mm) and the column (inside diameter 100 mm). At the top of the column, a simple T-junction was fitted with gas inlet 10 cm upstream of the orifice (hole diameter = 0.4 cm). The liquid recirculation was manually adjusted by a flow meter, while the hydrogen line was connected to a hydrogenation control unit to monitor consumption rate. The feed tank also acted as an intermediate tank during loop operation with a total capacity of 15 l. A cooling coil was installed in the intermediate vessel to provide isothermal conditions. All piping was made of stainless steel, except for gas lines.

When the DBC was operated in slurry mode, the monolith was removed from the column section leaving the

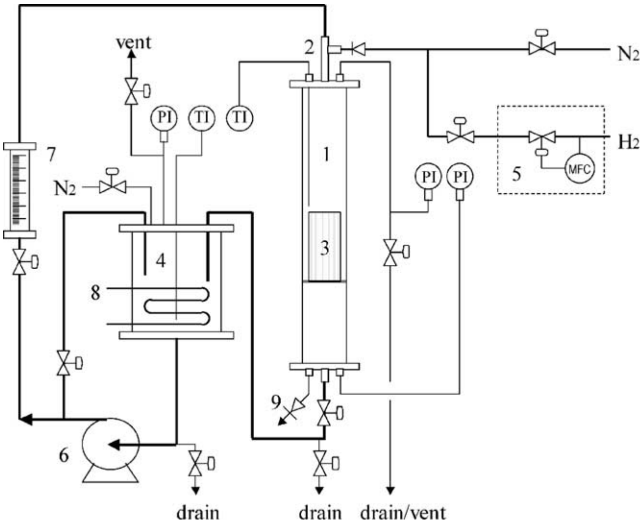

Fig. 2. Schematic experimental setup: (1) reactor column section; (2) T-junction with orifice outlet; (3) monolith; (4) feed/intermediate tank; (5) hydrogenation control unit with recorder; (6) centrifugal pump; (7) liquid flow meter; (8) cooling line; (9) pressure relief valve.

column empty. The powder catalyst used for slurry mode operation was 5% palladium on activated charcoal (average particle size of 19 μm) supplied by Johnson Matthey & Co. Ltd. (UK). For the conventional fixed bed catalysts, the palladium was coated on 16 mm α-alumina Norton Raschig rings (ICI-Katalco, UK) at the same loading as the monolith. The Pd-on-Raschig rings were randomly packed in the column and occupied 37 cm of column height.

A 10 l mixture of butyne-1,4-diol (Aldrich, UK) in 30% (v/v) 2-propanol–water was prepared and then charged to the feed tank. After flushing the system with nitrogen, the working solution was passed to fill up the column and recirculated until the working temperature was reached. Then, the gas supply valve was opened and hydrogen gas (BOC Ltd., UK) was allowed to be sucked according consumption rate by absorption and reaction. The height of gas–liquid dispersion was adjusted by control of the hydrogen supply with the caution that the liquid flow rate is still enough to maintain proper operation of the reactor. During shutdown, the monolith was kept in water. Similar procedure was also followed for operations in slurry and fixed bed mode.

The reaction progress was observed through product analysis by a gas chromatograph (Type 94 Ai-Cambridge, UK) and the change in hydrogen uptake measured by a hydrogenation control unit. The GC analysis was carried out using a flame ionisation detector and a DB-Wax capillary column (30 m long and 0.25 μm of film thickness) made by J&W Scientific (UK). No sample preservation was required.

3. Results and discussion

3.1. Analysis of initial reaction rates in the monolith DBC

The initial hydrogenation rates in the Pd-monolith DBC were measured at different temperatures, pressures and initial butyne-1,4-diol concentrations, and then analysed for the reaction kinetics. It is presumable that the conversion of butyne-1,4-diol to *cis*-butene-diol is the only reaction takes place since previous work has revealed that high selectivity (more than 95%) was observed up to 100% butyne-1,4-diol conversion [6].

The temperature dependence of the reaction rate was analysed using an Arrhenius type plot. The calculated values of apparent activation energies were 11.5 and 11.2 kcal/mol at pressures of 2–3 bar hydrogen, respectively. Indeed, these values are comparable with the observed values in the stirred tank reactor (STR) and the slurry DBC [7]. This fact suggests that the rate observed in the monolith DBC reactor is close to the intrinsic reaction rate, which means that the hydrogenation of butyne-1,4-diol is controlled by the surface reaction.

The initial hydrogenation rate as a function of hydrogen partial pressure is presented in Fig. 3. It shows a linear relationship, and clearly suggests that the reaction was first order kinetic with respect to hydrogen partial pressure. A similar observation was reported in the literature [8,9].

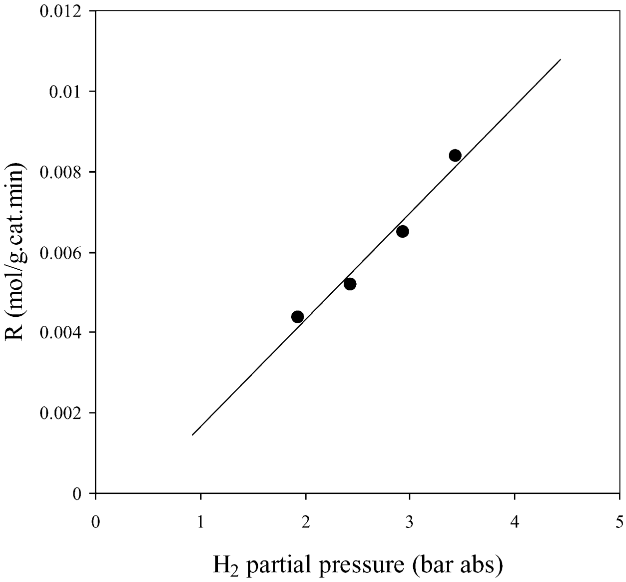

Fig. 3. Effect of hydrogen partial pressure on initial reaction rate (C_B = 0.1162 mol/l, T = 308 K).

The effect of the initial concentration of butyne-1,4-diol as a substrate on reaction rate is shown in Fig. 4. It is surprising to observe that the reaction rate in the monolith DBC was related by a positive order with the variation of butyne-1,4-diol concentration. It was reported previously that in the stirred tank reactor and the slurry DBC, the reaction order in butyne-1,4-diol was negative showing a substrate inhibition effect on the rate [7]. Other researchers found that the order was also negative [9,10], but Rongfu and Qiwei [8] reported zero order with respect butyne-1,4-diol in the reaction using a Raney nickel catalyst, a less active catalyst compared with the palladium.

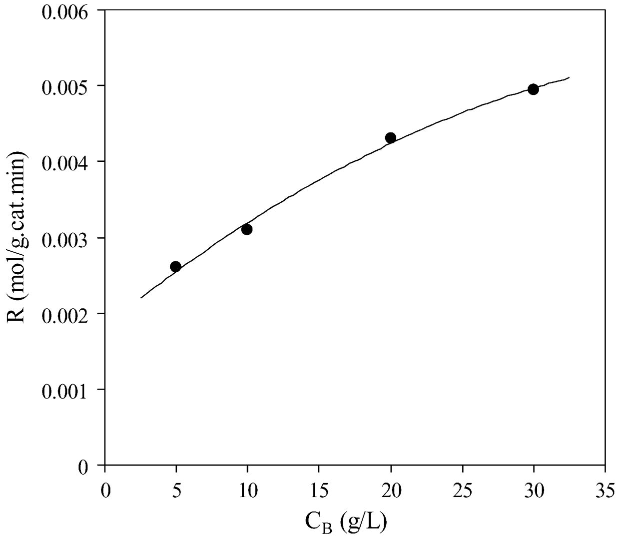

Fig. 4. Effect of initial butyne-1,4-diol concentration on reaction rate (T_C = 308 K, P = 3 bar abs).

The positive order with respect to butyne-1,4-diol could be due to a significant improvement in hydrogen mass transfer rate. The inhibition observed in the STR and the slurry DBC resulted from a competitive adsorption between butyne-1,4-diol and hydrogen with the former much more strongly adsorbed onto the catalyst surface. In the monolith DBC operated with two-phase or Taylor flow, improved hydrogen transport was possible, as the interface between bubbles and the channel wall was very thin (10.7–12.5 μm), thus, the length of the diffusion path was very short. In addition, the interfacial surface area at both gas–liquid and liquid–solid interface in the monolith was also very high ($1600\ m^{-1}$).

The use of downward flow in the monolith DBC also contributed to mass transfer enhancement, since the tendency of bubbles to rise-up in the downward bubble flow inside the channels promoted bubble circulation which also increased liquid film turbulence. As a result, the increased liquid film turbulence improved hydrogen mass transfer to the catalyst. It can be concluded that an increased hydrogen mass transfer in the monolith channel increased the possibility of hydrogen adsorbing on the catalyst surface in competition with butyne-1,4-diol and remarkably resulted in the reaction being of a positive order with respect to butyne-1,4-diol concentration. Certainly, it gives a further possible application of the monolith DBC in the field of process intensification since the problem of substrate inhibition found in other reactor types can be overcome in the DBC incorporated with the monolith catalyst.

3.2. A comparison with the slurry and fixed bed DBC

Fig. 5 shows that the reactions in the monolith DBC occurred at significantly higher rates than those observed in the fixed bed DBC operated at high interaction regime (similar flow condition reported by Boyes et al. [11]), made on the basis of palladium metal weight in the reactor. Poor distribution of gas–liquid dispersion over the catalysts of the fixed-bed DBC seems to contribute to lower rate in the reactor. The reaction rates in the slurry mode, however, were higher than those in the monolith DBC due to the use of fine catalyst particles in the slurry mode. In this case, the advantage of the monolith DBC over the slurry one was to immobilise catalytic material, hence avoiding the catalyst separation problem associated with the slurry operation. Another constraint of the slurry mode was a limited catalyst loading to be employed due to the problems of pumping and catalyst settling. This allows the monolith DBC to be a more compact reactor than the slurry reactor since it can employ a higher catalyst loading per reactor volume, hence giving a faster reaction rate. The monolith catalyst used in this work contained $2.132\ kg$ Pd metal m^{-3} of bulk volume of the monolith, while the Pd-on-charcoal catalyst at loading of $0.75\ kg\ m^{-3}$ (the highest used in the slurry type reactor) provided $0.0375\ kg$ Pd metal m^{-3} of reaction volume. Hence theoretically, the rate per reaction volume in the monolith DBC would be much higher than that in the slurry DBC. Fig. 6 revealed the fact that the reaction rate in the monolith higher than in the slurry. However, the ratio of rate enhancement was not increased accordingly with the ratio of metal content between those two reactors, due possibly to a non-optimum palladium distribution in the channels of the monolith.

The activation energy of the reactions in the monolith DBC were found higher than $10\ kcal\ mol^{-1}$, suggesting that the reactor operated in the kinetic control regime, similar to those found in the cases of the slurry DBC [7]. It indicates that the monolith DBC was able to maintain the rate control regime in the kinetic region even though a much higher metal content was used. This could be due to a very short

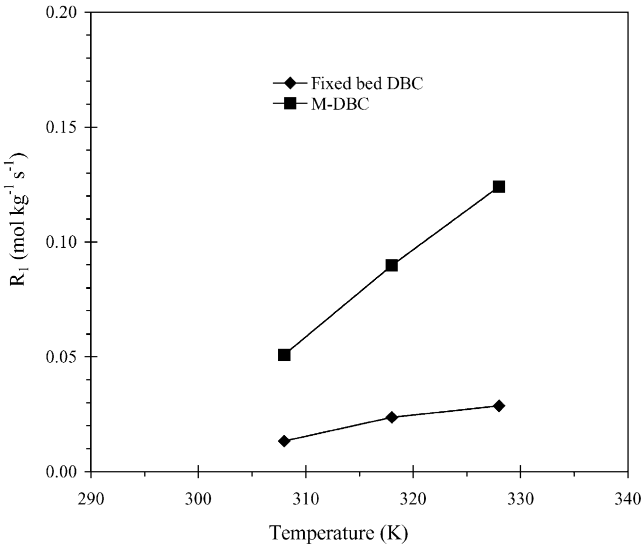

Fig. 5. Reaction rates in a fixed bed DBC and the monolith DBC (based on mass of Pd).

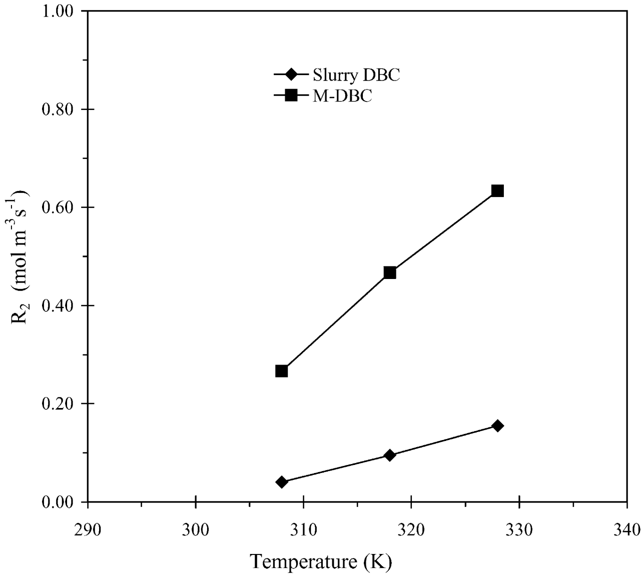

Fig. 6. Reaction rates in a slurry DBC and the monolith DBC (based on reaction volume).

diffusion length from the gas plug to the catalytic material hence eliminating intraparticle diffusional and liquid–solid mass transfer resistances, which are commonly problems associated with the conventional fixed bed reactor. Since the direct hydrogen mass transfer was likely to occur between the gas plug to the catalyst, rather than through the liquid plug, the problem of gas–liquid mass transfer was also negligible. In addition, in the DBC reactor, it is believed that the liquid was saturated with hydrogen before entering the monolith section as the results of two-phase vigorous mixing and turbulence in the entry zone of the DBC and then in the bulk dispersion region. All these ensured that the liquid plug was maintained at its hydrogen-saturation level during the passage throughout the channels of the monolith.

Fig. 7 presents a selectivity comparison observed in the monolith DBC, slurry, and fixed bed DBC reactors operated at the same reaction conditions. The selectivity towards *cis*-butene-1,4-diol in the monolith DBC indicates the values which were similar to those in the fixed bed DBC, but significantly better than those in the slurry DBC. Although the slurry mode DBC also has the element of plug flow behaviour [12], it seems that the characteristics of a close approach to plug flow in the monolith DBC [6], and also in the fixed bed DBC, have enhanced the selectivity of this reaction further compared with the slurry reactions.

3.3. Reaction kinetics

The kinetics of the hydrogenation of butyne-1,4-diol can be represented by a Langmuir–Hinshelwood type of rate reaction assuming that the rate-determining step is the surface reaction of adsorbed dissociative hydrogen and adsorbed butyne-1,4-diol [7]:

$$\mathrm{by}\cdot\mathrm{s} + 2\mathrm{H}\cdot\mathrm{s} \rightleftarrows \mathrm{be}\cdot\mathrm{s} + \mathrm{s} \qquad (1)$$

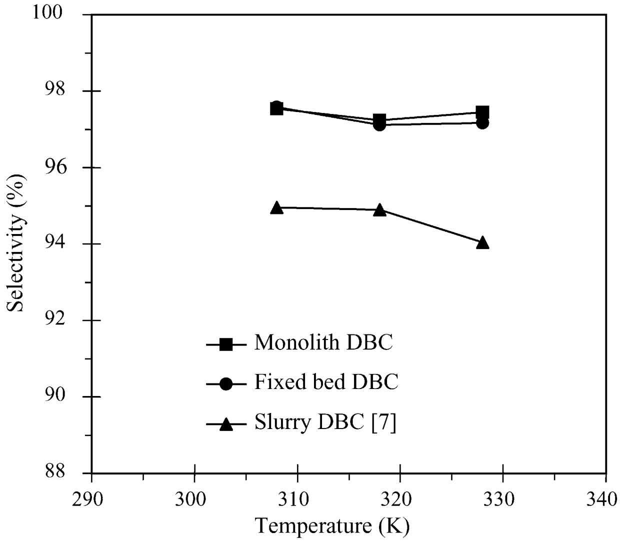

Fig. 7. A comparison of selectivity observed in the monolith, fixed bed and slurry DBC.

Table 1
Values of reaction rate and adsorption constants for parameters of the kinetic equation

Reactor	k	K_{by}	K_{H}
Slurry DBC	5.07	5.30	2.33
Monolith DBC	21.00	1.57	1.31

where by · s is the adsorbed butyne-1,4-diol, H · s the adsorbed hydrogen atom, be · s the adsorbed butene-1,4-diol and s the active site of the catalyst. Therefore, the surface reaction rate occurred can be expressed as follows:

$$r = k\theta_{\mathrm{by}}\theta_{\mathrm{H}}^{2} \qquad (2)$$

where θ_{by} and θ_{H} are the fractional coverage of the adsorbed butyne-1,4-diol and the adsorbed hydrogen atom, respectively. Previous work [7] also concluded that butyne-1,4-diol and hydrogen are adsorbed competitively on the same sites. In addition, butyne-1,4-diol is much more strongly adsorbed over palladium than the main reaction product butene-1,4-diol. As the result, the following rate equation is readily derived:

$$r = \frac{kK_{\mathrm{by}}K_{\mathrm{H}}C_{\mathrm{by}}C_{\mathrm{H}}}{(1 + K_{\mathrm{by}}C_{\mathrm{by}} + K_{\mathrm{H}}^{1/2}C_{\mathrm{H}}^{1/2})^{3}} \qquad (3)$$

where K is adsorption equilibrium constant. The hydrogen concentration on the active surface was assumed equal to the saturation degree since the liquid phase itself has been saturated and the possibility of direct hydrogen transport to the catalyst surface. The parameters of the model (k, k_{H2} and K_{B}) were predicted by a non-linear least squares regression, for which the residual sum of squares was minimised by the Nelder–Mead method [13] with the confidence limit of 95%. The magnitude of the parameters shown in Table 1 suggested a different kinetic behaviour between the monolith DBC and the slurry one. The reaction rate constant was found higher in the M-DBC than that of in the slurry one, while the

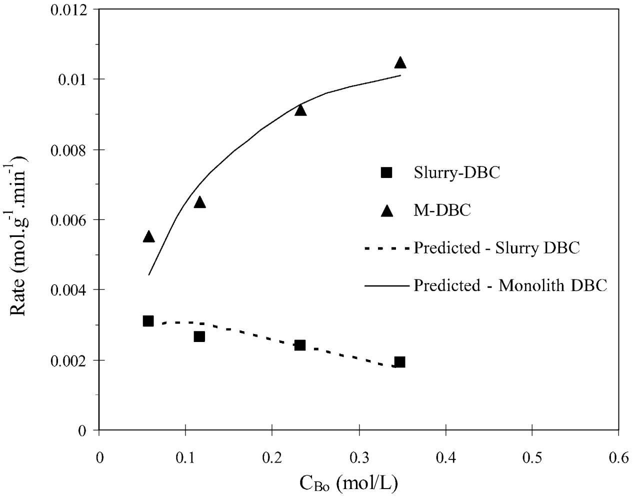

Fig. 8. Experimental and predicted reaction rate vs. butyne-1,4-diol concentration in the monolith (M) and slurry (S) DBC.

adsorption constants for the two reactants were rather similar. The proposed kinetic model describes the experimental data quite satisfactory as shown in Fig. 8.

4. Conclusion

It is concluded that the monolithic DBC used for hydrogenation of butyne-1,4-diol was close to a reactor featuring a concept of clean technology, which also includes process intensification aspect. In terms of process intensification, no doubt, the monolithic DBC facilitates a very high reaction rate due to the possible use of much higher catalyst content per reaction volume without the diffusional resistance problems. In addition, compared with the other types of monolith reactor reported in the literature, the monolithic DBC was so simple due to its inherent characteristic operation and no specially designed distributor. The reaction rates and the selectivity towards *cis*-butene-1,4-diol in the monolith DBC were found significantly better than those in the slurry and fixed bed operation mode of DBC. The reaction kinetics based on the Langmuir–Hinshelwood mechanism was developed in a good agreement with the experimental data.

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