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Monolith loop reactor for hydrogenation of glucose

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ABSTRACT

Monolithic and powder catalysts based on Ru on γ-Al_2O_3 for hydrogenation of glucose to sorbitol were prepared and shown to have comparable physico-chemical properties. Monolithic catalysts were investigated in a loop reactor in the Taylor Flow regime. For this purpose an experimental setup was built, where gas and liquid can be recycled independently. For comparison of monolithic and powder catalysts, a stirred tank reactor is integrated in the setup. Analysis of hydrogenation experiments revealed that external mass transfer limitations occur in case of the powder catalyst, whereas the monolithic catalyst used in the present study suffers from internal mass transfer resistances. Monolithic catalysts with sufficiently thin catalyst should be a promising alternative to suspended powder catalysts as they allow for an improvement of overall reaction rates.

1. Introduction

The hydrogenation of glucose (Eq. (1)) is a heterogeneously catalyzed reaction for producing the sugar alcohol sorbitol, which is an important industrial product with a world capacity of more than 1 Mt/a.

$$C_6H_{12}O_6 + H_2 \xrightarrow{+\text{catalyst}} C_6H_{14}O_6 \quad (1)$$

Sorbitol is used as sugar substitute and low calorie sweetener in foods and candies especially for diabetics, as humectant and softener in cosmetic and pharmaceutical products, and as an intermediate for the production of vitamin C [1].

The hydrogenation of glucose is mainly carried out in discontinuously operated stirred tank reactors with suspended powder catalysts at temperatures of 393–423 K and pressures of 40–180 bar. The use of continuously operated trickle-bed reactors is less common in industry [2]. In most cases Raney nickel catalysts are used for this reaction due to the relatively low price and high sorbitol selectivity. On the other hand, nickel based catalysts exhibit strong leaching and deactivate relatively fast. Especially for applications in food, cosmetics and pharmaceuticals the nickel has to be removed by ion exchange resulting in additional costs [3].

Other active materials were investigated for glucose hydrogenation in several studies. Among these materials, especially supported ruthenium catalysts show promising catalytic properties. Although ruthenium is much more expensive than nickel, it might be of interest for industrial use as it is more active than nickel and shows no leaching [1,4]. However, the use of suspended ruthenium based catalysts in traditional stirred tank reactors is challenging as the low density of supported ruthenium catalysts compared to Raney nickel slows down the catalyst sedimentation between batches and creates costs for larger filtration capacity [3,5].

Another disadvantage of suspended catalysts in stirred-tank reactors is the occurrence of mass transfer resistances especially at higher temperatures and glucose concentrations [6,7]. Reactors with structured catalysts like honeycomb monoliths are an interesting alternative to established reactors with conventional catalyst geometries. The catalyst is fixed on monolithic honeycomb carrier structures so that no intricate filtration step is required. These structures also offer high specific surface area and excellent mass transfer properties at low pressure drop. A monolithic catalyst could be relatively easily integrated in an existing stirred tank reactor by an external loop of gas and liquid. Other possible configurations with internal recycles are also described in the literature [8,9].

First experimental investigations have successfully shown the feasibility of monolithic catalysts for hydrogenation of glucose [3]. These investigations have been carried out in a stirred tank reactor as well as in a loop reactor with a hydrogen saturated glucose solution. However, the full potential of monolithic catalysts could not be exploited in this experimental setup, since the Taylor flow regime with particular efficient mass transfer characteristics was not realized.

The present contribution deals with a novel laboratory reactor concept for investigation of glucose hydrogenation according to a

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loop-reactor concept that has been demonstrated for Fischer–Tropsch synthesis [9,10]. In this setup, monolithic catalysts are investigated in a tubular reactor with independent recycle of gas and liquid, which allows for adjustment of the preferred slug flow regime inside the monolith honeycomb channels. For the experimental investigations Ru-Al_2O_3 catalysts were prepared both as powder and as thin layer deposited on a monolith honeycomb carrier structure. It will be shown that both catalyst geometries exhibit very similar physical and chemical properties. First experimental results show that the novel setup is suitable for the investigation of monolithic catalysts in the Taylor flow regime. Comparison with results over powder catalysts reveal that overall reaction rates can be intensified by using monoliths, especially through much better external mass transfer properties.

2. Catalysts preparation

Most previous studies of ruthenium based catalysts for glucose hydrogenation employed carbon as support. Although methods for preparation of carbon-coated monoliths have been described in the literature [11], it appears difficult to obtain catalysts in different geometries with comparable physical and chemical properties with these methods [3]. For this reason, monolithic and powder catalysts with 8 wt% ruthenium on γ-Al_2O_3 were prepared (Fig. 1) according to a method described by Guettel et al. [10]. In a first step, a catalytic base powder was prepared (A). This catalytic base powder and a binder material were suspended in water (B). In the following step, this suspension was used to coat the monolith carrier by dip coating (D) and to obtain the powder catalyst through drying and calcination of the suspension (C). Details of the procedure are described below. In a solution of 60.0 g ruthenium nitrosylnitrate (Alfa Aesar) in 600 mL deionized water, 247.6 g of dried alumina powder (γ-Al_2O_3, 5 μm, Puralox UF 5/230, Sasol) was suspended. This suspension was dried at 90 °C, heated to 350 °C with a heating rate of 2 K/min and finally calcined for 4 h at 350 °C in air. For the dip coating process 45 g of the catalytic base powder was suspended in a mixture of 115 g deionized water (adjusted at pH 5 with nitric acid) and 25.7 g of colloidal alumina binder (pseudo-boehmite, 20 wt%, 50 nm, Alfa Aesar). The suspension was dispersed with an ultrasonic sonotrode (2 min, 75 W).

Monolith pieces (cordierite, 400 cpsi, Corning) with a diameter of 12 mm and a length of 50 mm were used as carrier and dipped into the suspension for 1 min. The excess of the suspension was gently removed by pressurized air. The coated monoliths were dried for 4 h at 90 °C, heated to 350 °C with a heating rate of 2 K/min and subsequently calcined for 4 h at 350 °C in air. The coating procedure was repeated several times to obtain the desired washcoat mass fractions and the resulting catalyst layer thickness. The powder catalyst was prepared using the slurry by drying (4 h at 90 °C) and calcination in air (4 h at 350 °C, heating rate 2 K/min). The resulting powder was crushed and sieved to the desired fraction. To improve the mechanical stability of the catalysts, both powder and monolithic catalysts were subjected to an additional calcination step in air for 16 h at 600 °C.

During development of the dip-coating method, the zeta potential of slurries with different pH was measured with a nano-ZS zeta sizer (Malvern Instruments). The final catalysts were analyzed by several physico-chemical methods. The Brunauer–Emmet–Teller (BET) surface area and pore size distribution were determined by nitrogen adsorption with the Barrett–Joiner–Halenda (BJH) method. X-ray diffraction (XRD) measurements were used to identify the phase structures and scanning electron microscopy (SEM) was employed to estimate the layer thickness of the washcoat. For temperature-programmed reduction (TPR) catalyst samples (~50 mg) were pretreated for 30 min in a flow of helium (20 mL/min, NTP) at 120 °C. After cooling down, the samples were heated with 10 K/min from 50 to 500 °C in a flow of 10% H_2 in argon at atmospheric pressure. Pulsed chemisorption measurements with hydrogen were performed to measure dispersion, metal surface area and mean cluster size. The samples (~75 mg) were reduced in a flow of 10% H_2 in argon (20 mL/min, NTP) for 60 min at 200 °C. After cooling down the pulsed chemisorption was performed at 50 °C with 10% H_2 in argon. For calculating the Ru surface area a stoichiometric ratio of $Ru/H_2 = 2$ was assumed [6]. For both TPR and pulsed chemisorption measurements a BELCAT-M (BEL Japan, Inc) catalyst analyzer was used.

3. Hydrogenation experiments

Hydrogenation experiments were carried out to compare reaction rates of powder and monolithic catalysts during glucose hydrogenation. The powder catalyst was crushed and sieved to a fraction of 63–120 μm and reduced in an external furnace. After heating in a flow of N_2 at atmospheric pressure with a ramp of 1 K/min from room temperature to 200 °C the powder catalyst was kept for 12 h in a flow (40 mL/min, NTP) of 10% H_2 in N_2. After reduction the catalyst was cooled in N_2 to room temperature, covered with glucose solution to prevent reoxidation and directly transferred to the autoclave. The monolithic catalyst was reduced under the same conditions as the powder catalyst directly in the loop reactor setup.

The experimental setup combines a stirred tank reactor with a tubular reactor according to the external loop reactor concept (Fig. 2). This setup allows the investigation of both the powder catalyst in a slurry stirred tank reactor and the monolithic catalyst in a tubular reactor. The stirred tank reactor with a volume of 4 L was equipped with a gas injection stirrer. The tubular reactor with an internal diameter of 14 mm and a length of 1000 mm used a sieve plate for distribution of gas and liquid phase at the top and a perforated plate at the bottom as suggested in the literature [12]. The autoclave was heated by heat carrier oil while the tubular reactor was electrically heated.

The experiments in the stirred tank reactor were carried out with 7 g of the powder catalyst and 1600 g of a glucose solution with 40 wt% glucose (D(+)-glucose anhydrous puriss, Sigma–Aldrich). Under hydrogen atmosphere at a pressure of 5 bar, the

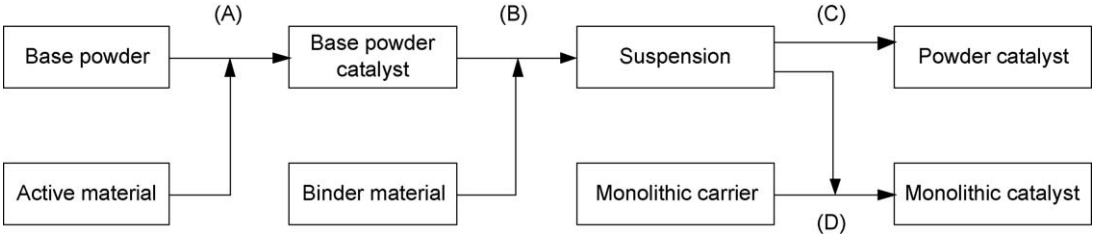

Fig. 1. Preparation steps for monolithic and powder catalyst.

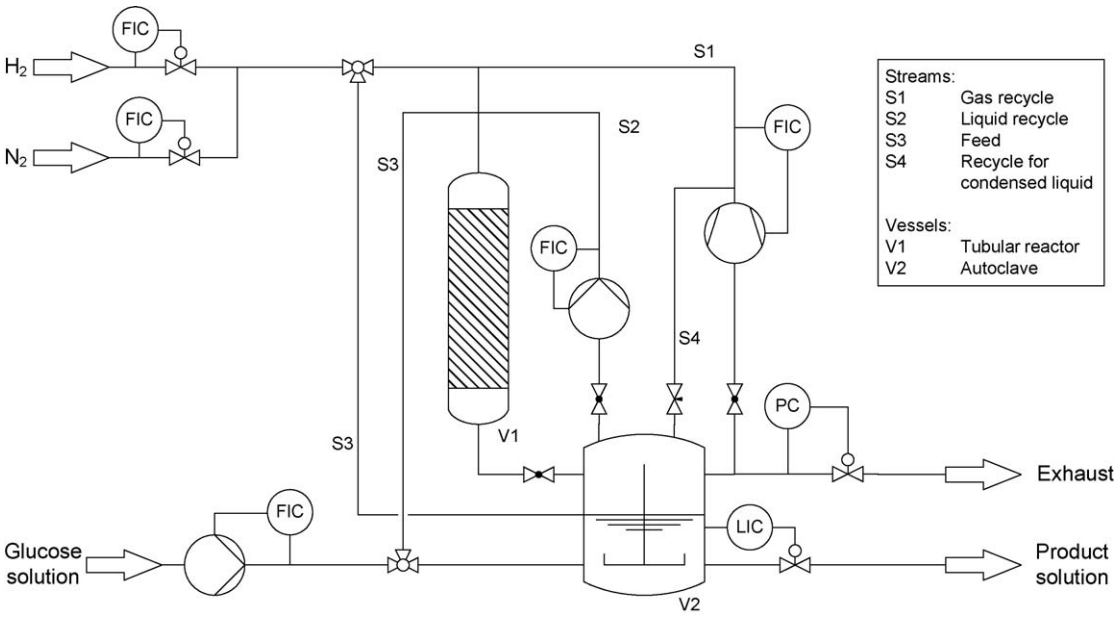

Fig. 2. Experimental loop reactor setup.

autoclave was heated up to the desired reaction temperature with a reduced stirrer speed of 250 min^{-1} to avoid reaction. At this stirrer speed there is little transport of gas to the liquid and the catalyst is hardly suspended, since no gas bubbles are formed by the gas injection stirrer. The experimental results reveal that the glucose conversion before increasing the stirrer speed can be neglected. After the temperature had been reached the pressure was raised to 80 bar. Directly after achieving the reaction pressure the stirrer speed was set to 1000 min^{-1} and this point of time was regarded as start of the reaction. The hydrogen pressure was kept constant by continuously feeding the consumed amount of hydrogen to the setup via a mass flow controller (Bronkhorst El-Flow). In this operation mode, the tubular reactor as well as gas and liquid recycle streams were disconnected from the stirred tank reactor.

For experiments with monolithic catalyst the stirred tank reactor is used as a phase separator for liquid and gas phase, while gas and liquid are recycled independently by using a compressor and a pump. The gas is transported by a compressor (Maximator DLE-15 GG) and the mass flow is measured by a coriolis mass flow meter (Rheonik RHM 15). The liquid is pumped with a gear pump (Gather Industrie) from the stirred tank reactor to the tubular reactor. The liquid mass flow is also measured by a coriolis mass flow meter (Rheonik RHM 04). About 10 g of active catalyst material fixed on the monolith carrier were used. Since 2300 g of a glucose solution with 40 wt% glucose were used, the ratio between catalyst and dry glucose mass (~1.1 wt%) is the same during experiments with monolithic and powder catalysts. At a hydrogen pressure of 5 bar the liquid recycle loop was operated at a superficial velocity of 0.1 m/s and the tubular as well as the stirred tank reactor were heated to the desired reaction temperature. A stirring speed of 500 min^{-1} was used in the autoclave. After reaching the temperature, which was measured by thermocouples at the top of and at the bottom of the reactor, the pressure was raised to 80 bar. Finally, the gas recycle stream was also set to a superficial velocity of 0.1 m/s to achieve the slug flow regime inside the monolith channels and this point of time was regarded as start of the reaction. During the hydrogenation experiment liquid samples were taken from the stirred tank reactor through a sampling line equipped with a needle and a magnetic valve. The samples (approx. 5 g) were analyzed offline using a HPLC equipped with an evaporative light scattering detector (PL-ELSD 2100). Separation of the components was achieved by a PL Hi-Plex Ca (300 mm × 7.7 mm) monosaccharide column (Polymer Laboratories) operated at 85 °C. For the mobile phase water was used at a flow rate of 0.6 mL/min. Glucose, fructose, mannitol and sorbitol were calibrated with sucrose as internal standard. In addition to the described discontinuous operation mode for monolithic and powder catalyst it is also possible to perform continuous hydrogenation experiments in this experimental setup by feeding liquid educt solution to the setup and removal of reaction mixture.

4. Results and discussion

4.1. Catalyst characterization

Initially, zeta potential measurements were carried out to determine the most suitable pH value for the dip-coating procedure. For this purpose the potentials of crushed monolith carrier particles and catalytic base powder particles were measured at different pH values between 1 and 12. The difference of zeta potentials for monolith carrier and catalytic base powder showed a maximum at pH 5, indicating a good adhesion between the washcoat and the monolith carrier at these conditions. Guettel et al. [10] determined an optimal pH value of 7 for a Co/Re catalyst while Christiani et al. [13] found pH 3.5 most suitable for pure aluminum oxide. Obviously, the kind of active material has a significant influence on the optimal pH value, which must be experimentally determined for every dip-coating procedure.

The mass fraction of the coated monoliths was measured gravimetrically. After six coating steps a mass fraction of about 22 wt% was reached. With each coating step the mass fraction of washcoat on the carrier increased almost linearly in contrast to observations described in the literature [10]. SEM investigation showed an uneven catalyst layer thickness, which is about three times thicker in the corner compared to the planar walls in the square monolith channels. Taking these differences into account, a characteristic diffusion length of the washcoat of 90 μm was calculated as described in the literature [10]. The characteristic diffusion length of 15 μm for the powder catalysts was estimated by assuming a spherical geometry with 1/6 of the mean particle

Table 1
Properties of monolithic and powder catalyst.

	BET surface area ($m^2 g_{cat}^{-1}$)	Pore volume v_p ($cm^3 g_{cat}^{-1}$)	Active surface area ($m^2_{Ru} g_{cat}^{-1}$)	Dispersion (%)	Mean cluster size (nm)
Powder catalyst	181	0.406	3.23 ± 0.11	11.2 ± 0.4	11.9 ± 0.4
Washcoat	169	0.394	3.32 ± 0.07	11.5 ± 0.2	11.5 ± 0.2

Table 2
Results of hydrogenation experiments at 80 bar.

	Characteristics diffusion length l_{char} (μm)	Initial observed reaction rate $r_{m,0}$ (mol kg_{cat}^{-1} s^{-1})		
		100 °C	120 °C	140 °C
Powder catalyst	~15	0.037	0.106	0.156
Monolithic catalyst	~90	0.021	0.045	0.097

diameter. Experiments with similar characteristic diffusion lengths for powder and monolithic catalysts are planned.

The XRD measurement showed phases of RuO_2, γ-Al_2O_3 and colloidal alumina binder present in the final powder catalyst. Table 1 summarizes the BET surface areas, the pore volumes and the results of pulsed chemisorption. The properties of the washcoat were calculated according to the literature [10]. The determined BET surface area for the washcoat is slightly lower than for the powder catalysts, although the cumulative pore volumes are very similar. Fig. 3a reveals that the pore size distributions of washcoat and powder catalysts are comparable. It can be seen that dispersion, active metal surface and mean cluster diameter for both catalyst geometries are almost equal. Fig. 3b shows the TPR profiles of the monolithic and powder catalyst, which are again in good agreement. The single peak is caused by reduction of RuO_2 [14]. Overall, the monolith washcoat and the powder catalyst have very similar properties so that both catalyst geometries are directly comparable.

4.2. Hydrogenation experiments

From the measured concentration–time profiles the catalyst mass specific initial reaction rates $r_{m,0}$ were calculated (Table 2). These initial reaction rates are quite different for powder and monolithic catalysts. An Arrhenius diagram (Fig. 4) for the powder catalyst shows an apparent decrease of the activation energy (E_a) at increasing temperature. Whereas the roughly estimated activation energy E_a between 100 and 120 °C is very similar to values described in the literature [6], the strong decrease at higher temperatures may be attributed to mass transfer resistances. On the other hand, the observed reaction rate for the monolithic catalyst is smaller than for the powder catalyst, which is in contrast to observations reported in the literature [5]. A possible and straightforward explanation could be internal mass transfer resistances caused by the much larger diffusion length of 90 μm

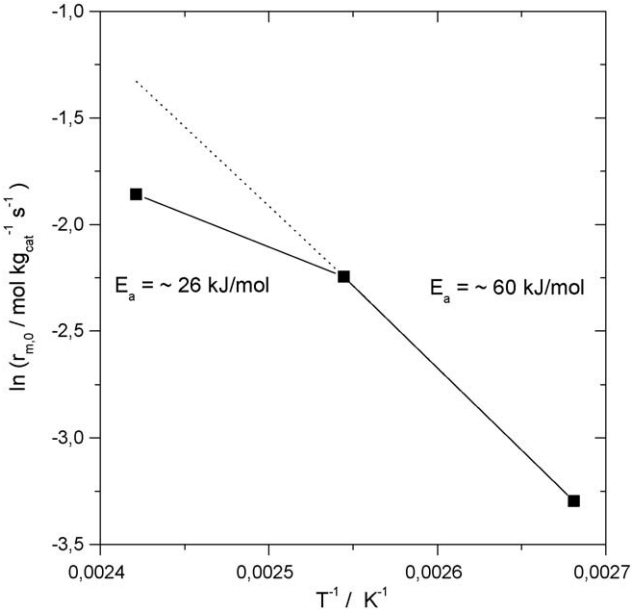

Fig. 4. Arrhenius diagram for experiments with powder catalyst.

in the monolith compared to 15 μm for the powder catalyst. To test this hypothesis, mass transfer coefficients in the slurry stirred tank and monolith reactor as well as the catalyst effectiveness factors were estimated. The required data and correlations were taken from [6,7,10,15].

From the time constants for mass transfer and reaction rate the time constant for the intrinsic reaction rate and an overall effectiveness factor can be calculated. The time constant for the observed reaction rate was obtained assuming a simplified first order reaction rate proportional to the H_2 concentration in the

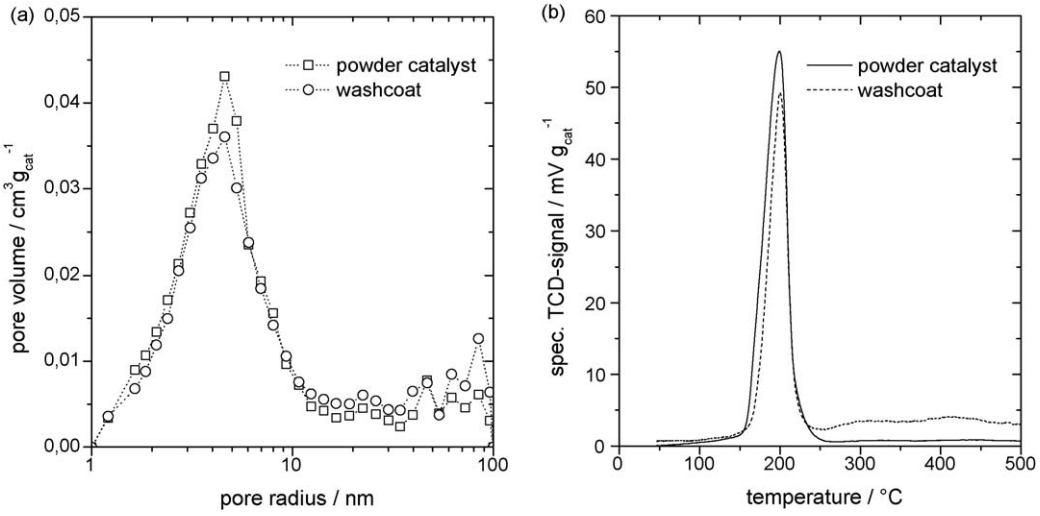

Fig. 3. Pore volume distribution and TPR profiles of monolithic and powder catalyst.

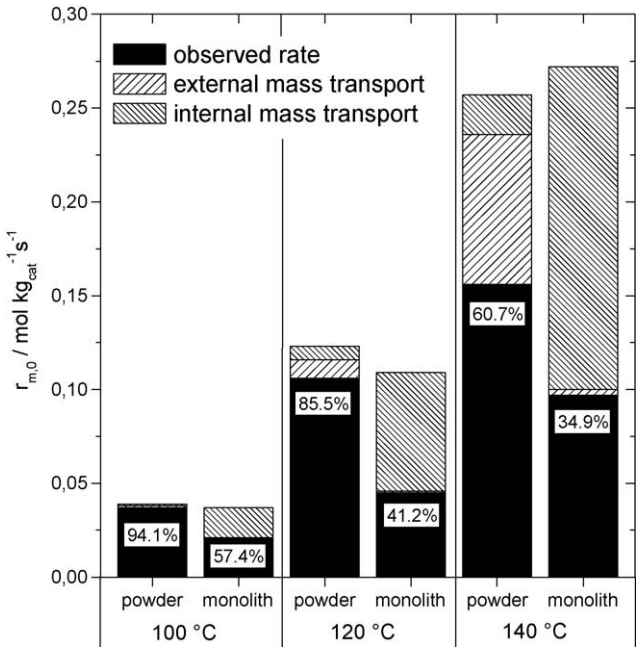

Fig. 5. Observed initial reaction rates, overall effectiveness factors and possible improvements in the absence of external and internal mass transfer resistances.

liquid. Fig. 5 shows that mass transfer resistances affect the observed reaction rates. Although these calculations are rough, the resulting intrinsic reaction rate constants for powder and monolithic catalyst are in good agreement. The estimated activation energy of ~62 kJ/mol is close to values describes in the literature [6,7], which supports the presented approach. The monolithic catalyst at the given thickness of the washcoat layer is strongly influenced by internal mass transfer resistances, while the powder catalyst is to a larger extent influenced by external mass transfer resistances. The negative influence of internal mass transfer resistances on the reaction rate of the monolithic catalyst, which has also been described in the literature [3], can be reduced easily by employing monoliths with lower washcoat layer thickness. On the other hand, improvement of the external mass transfer rates in the slurry stirred tank reactor is very difficult. These first investigations show that a suitable monolithic catalyst with a sufficiently thin washcoat layer should allow for intensifying the mass-specific reaction rate by a factor of approx. 1.5 at 140 °C and 80 bar. Future experiments will be targeted at experimental verification of these estimations.

5. Conclusion

Monolithic and powder catalysts for glucose hydrogenation based on ruthenium (~8 wt%) on γ-Al_2O_3 have been prepared. The monolithic catalyst was obtained by a repeated dip-coating procedure and the powder catalyst was received from the same slurry was used for dip-coating. Both catalysts show very similar physico-chemical properties. Monolithic catalysts in a loop reactor were compared to powder catalysts in a stirred tank reactor. It could be shown that the powder catalyst suffers from external mass transfer resistances especially at higher temperatures whereas the monolithic catalyst exhibits intensified external mass transfer rates due to the advantageous slug flow regime. However, the monolithic catalyst used in the present study was influenced by internal mass transfer resistances caused by large diffusion lengths inside the catalytic washcoat layer. Estimations of the influence of internal and external mass transfer resistances on the observed reaction rate show that it should be possible to outperform the activity of the powder catalyst by reducing the washcoat layer thickness and thus the internal mass transfer resistances for the monolithic catalyst. As further improvement of the external mass transfer rate for the powder catalyst seems not to be feasible and the challenge of catalyst separation remains, a properly designed monolithic catalyst could be an interesting alternative to suspended powder catalysts for glucose hydrogenation to sorbitol.

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