Application of monoliths in packed bed and stirred tank reactors

Brishti Mitra , Department of Chemical Engineering, University Institute of Engineering and Technology, CSJM University,
Email: dr.brishti.mitra@gmail.com

Abstract

Monoliths, also known as structured catalyst reactors, have gained increasing attention in recent years due to their advantages of conventional packed bed and stirred tank reactors. Monoliths have been coated with various catalytic materials, including metals, oxides, and zeolites, making them versatile and adaptable for a wide range of reactions. The application of such reactors is studied for two reactions – disproportion of toluene in a zeolite coated monolith two-phase plug flow reactor and hydrogenation of 2-butyene-1, 4-diol with palladium on alumina coated monoliths in a three-phase stirred tank reactor. In both cases, monolith reactors can be successfully applied and product conversion and selectivity can be controlled by altering the thickness of the zeolite washcoat.

Keywords: monolith, washcoat, plug-flow configuration, stirred tank reactor

Introduction

Structured reactors, specifically monoliths, have been utilized in the chemical industry for several decades. The term "monolith" originates from Greek , means a large uniform block of a single building material with thin, vertical, parallel channels separated by walls. Monoliths are commonly used in heterogeneous catalysis as a support or integral component of a catalytically active material [1].

Monoliths have been extensively used as small-scale reactors for combustion and emission control, with the catalytic converter in cars being a prime example. Furthermore, monolithic catalysts have been investigated for gas-solid reactions such as partial oxidation, steam reforming of hydrocarbons, autothermal reforming, and dehydrogenation of ethylbenzene, while their potential in gas-liquid reactions such as catalytic hydrogenation and oxidation is also being explored [2-4].

Conventional fixed bed reactors have several drawbacks, including maldistributions of various kinds, which can be addressed by using structured catalysts. A monolithic reactor has several advantages over other types of reactors. The narrow pores of the channels with a thin coating of the catalytically active material and the high geometric surface area of the monolith enhance the contact between the gas and the catalyst, resulting in high conversion and selectivity. The open structure of the monolith and the low resistance to the gas flow reduce the energy consumption and the operating cost of the reactor. The monolith can withstand high temperatures and thermal shocks without cracking or deforming, which is important for reactions that involve exothermic or endothermic heat effects. The monolith can be easily fabricated in different sizes and shapes to fit different reactor configurations and capacities. Though monolith catalysts have been mostly used in gas-solid reactors under plug flow conditions, there are some processes where monoliths have been used in stirred tank reactors. The production of hydrogen peroxide is an industrial application of monolithic catalysts in multiphase processes [5]. The use of monoliths in stirred tank reactors offers several advantages over traditional packed bed catalysts. First, monoliths have a higher surface area per unit volume than packed beds, which allows for more efficient catalyst utilization and higher conversion rates. Second, the open channel structure of monoliths provides better mass transfer and lower pressure drop compared to packed beds, resulting in improved reactor performance. Third, the uniform distribution of reactants over the monolith channels results in a more homogeneous reaction environment, which can lead to better selectivity and higher yields.

Here, the preparation methods of monolith catalyst used in gas-solid and gas-liquid-solid reactions will be briefly discussed. Further, reaction studies will be carried out to demonstrate the applicability of monolith catalysts for two-phase and three-phase reactions. Xylene isomers produced from the disproportionation of toluene to is a commercially important reaction. p-Xylene is an important chemical compound that is primarily used as a feedstock in the production of terephthalic acid (TPA), which is a key component in the production of polyethylene terephthalate (PET) [6]. Also, catalytic hydrogenation of 2-butyene-1, 4-diol has

been selected as the test reaction which is an industrially important reaction for the production of endosulfan [7], vitamin A and B_6 [8]. The disproportionation of toluene will be carried out on zeolite washcoated monoliths in a plug flow reactor while the catalytic hydrogenation of 2-butyene-1, 4-diol will be carried out in a monolithic stirred tank reactor. In both cases, the objective would be to study the effect of thickness of the catalytic washcoat layer on conversion and selectivity.

Experimental

Catalyst preparation

Catalyst preparation for toluene disproportionation reaction: Monoliths washcoated with ZSM5 zeolite were prepared with loading ranging from 10-60 wt% to study the disproportionation of toluene in a plug flow reactor. Cordierite monoliths were used as catalysts supports The monoliths had 400 cells per square inch (cpsi) with an average wall thickness of 0.19 mm. Small sections of these monoliths were prepared by core-drilling of large blocks. The monolith pieces were approximately 1.95 cm in diameter and 3 cm in length. These sections were then washcoated with a slurry of ZSM5. Prior to washcoating, the monoliths underwent pretreatment at 873 K for 2 hours to eliminate any adsorbed impurities. The ZSM5 powder, with an average particle size of 2-3 μm, was wet ball-milled to prepare the slurry. An uniform slurry of 30 wt% concentration was prepared by ball-milling the required amount of ZSM5 powder with demineralized water. The monoliths were dipped vertically into a 30 wt% aqueous slurry for 3 minutes and then taken out of the solution. The excess slurry in the monolith channels were removed by air blowing. The coated samples were dried at 383 K for 2 hours, weighed, and the coating process was repeated to reach the final desired loading. For this study, the washcoat loadings prepared ranged from 10 to 60 wt% of ZSM5. Finally, the samples were calcined at 823 K for 4 hours, using a slow heating rate of 2 K/min to avoid any cracking of the washcoated layer. The stability of the washcoat is an important property and the weight loss during ultrasonication was measured to determine the adherence of the ZSM5 washcoat. The washcoated monoliths were immersed in acetone and subjected to ultrasonication (33 Hz) for 1 hour [9].

Catalyst preparation for hydrogenation of 2-butyene-1, 4-diol: Monoliths, made of cordierite, with a surface area of 0.6 m^2/g were used in this study. Cylindrical monolith pieces of dimension 17 mm diameter and 18 mm length and cpsi ranging from 200 to 400 were used as catalyst base. To enhance the surface area of the monolithic blocks, γ-alumina was chosen as the catalyst support and pseudoboehmite was used as a precursor. The precursor was calcined at 550 ^{0}C for 12 h and particle size of calcined pseudobomite was reduced by ball milling for 24 hours at 140 rpm. After milling, the solution was dried in an oven at 110 ^{0}C for 24 hrs and the powder was stored as stock for the slurry coating.

Slurry for washcoating was prepared by milling the required amount of milled calcined pseudoboehmite powder with water for 1h. Prior to the coating, bare monoliths were calcined at 600 ^{0}C for 1 hr to remove any adsorbed material from the surface. Monolith samples were dipped in the slurry such that slurry rose in the channels by capillary action. The monoliths were removed from the slurry after 3 min and the excess slurry was then removed by blowing air. The monoliths were kept in air for 30 minutes and subsequently the coated samples were dried at 110 ^{0}C for 2 h and then calcined at 500 ^{0}C for 5 h. Loading percentage was determined from the increase of specimen weight after calcination.

The active metal for the reaction, palladium was impregnated on the washcoated monoliths by wet impregnation method. Palladium chloride ($PdCl_2$) was used as the precursor. Washcoated monoliths were dipped in an aqueous solution of $PdCl_2$ of known concentration (generally 3.2 x 10^{-4} g/cc) for 24 hrs. Drops of dilute HCl (0.1 N) were added for complete dissolution of the salt. The monoliths were then taken out and the remaining solution was kept for analysis. The concentration of the remaining solution was determined by UV spectrophotometer with the help of a calibration curve. The percentage loading was calculated based on concentration change of the solution before and after dipping [10].

In order to compare the slurry and monolith stirred tank reactor, powder palladium catalyst was prepared by impregnation method. Calcined pseudoboehmite powder was taken as the support

and palladium chloride ($PdCl_2$) was used as the precursor. Small quantity of dilute HCl (0.1N) was added to ensure complete dissolution of the precursor. Water was evaporated using a rotary vacuum evaporator maintained around 60-70^{0}C. The powder was then dried overnight at 110 ^{0}C and calcined at 400 ^{0}C for 4hr.

Reaction studies

Toluene disproportionation reaction in plug flow reactor with powder, pellet and ZSM5 coated monoliths

The vertical stainless steel downflow reactor used for the toluene disproportionation reaction had a diameter of 19.7 mm and a length of 320 mm. The reaction was performed at atmospheric pressure and a temperature range of 573-773 K. The ZSM5 washcoated monolith was placed inside the reactor after smoothening the outer surface for a tight fit. To initiate the reaction, liquid toluene was vaporized in a preheater at 473 K, mixed with hydrogen (with an inlet toluene partial pressure of 33.44 kPa), and then introduced into the monolith reactor. Prior to exposure to the reactant, the catalyst washcoat was pretreated in nitrogen at 823 K for 2 hours. The W/F$_{Ao}$ was adjusted between 5-20 g h/mol, and the reactions were carried out for monoliths with varying average washcoat thickness.

To test the ZSM5 powder (0.0125-0.0178 cm) and pellet (diameter: 0.15 cm; length: 0.6 cm) catalysts, a stainless-steel reactor (diameter: 0.7 cm; length: 55 cm) was utilized. To ensure an adequate bed height, the powder or pellet catalysts were diluted with quartz particles and placed on a bed of quartz wool.

The gaseous and liquid products were analyzed by gas chromatography using a FID detector with nitrogen as the carrier gas.

Hydrogenation of 2-butyene-1, 4-diol in slurry and stirred tank reactors with monoliths:

For catalytic hydrogenation using Pd/Al_2O_3 catalyst, the reaction was carried out in a high-pressure laboratory autoclave. The maximum reactor volume was 2 liters. The pressure, temperature and agitator speed rating of this autoclave were 8 atm, 300 ^{0} C, and 1000 rpm, respectively. It consisted of an inbuilt heater, cooling coil connected with a chiller, a pressure gauge, a thermocouple, a condenser, and a stirrer driven by magnetic coupling. The stirrer had a two six bladed impeller with an inclination angle of 30^0. The monoliths were tied in the reactor by fine wires to the cooling coil. For palladium studies, no setup for catalyst reduction was needed as the catalyst was reduced in-situ before the reaction.

For the Pd studies, the reduction was done in-situ at 50 ^{0}C. The required amount of catalyst was taken in 500 ml of isopropanol. The system was flushed with N_2 flow for an hour to purge any air. This is required because palladium is pyrophoric. The catalyst was reduced with hydrogen for 2 hrs at a stirring speed of 250 rpm. After the reduction, the reactant dissolved in 500 ml of solvent was added through the sampling port. The reactor was then pressurized with H_2 upto the required value. The stirring speed was kept constant at 400 rpm throughout the run. Runs for different operating conditions were taken to determine the intrinsic kinetics of the reaction. An identical procedure was followed when the monoliths were used as catalysts.

The reaction products were analyzed on a gas chromatograph using a Chromosorb-101 column (i.d.: 2 mm; length: 2m). The products were detected using a flame ionization detector (FID). For reaction studies of all reactors, the conversion of the reactant and selectivity of the products were calculated for each run. Conversion of reactant (%) and selectivity (%) of product i, are defined as:

$$Conversion\ (\%) = \frac{Initial\ moles\ of\ reactant - Moles\ of\ reactant\ in\ the\ product}{Initial\ moles\ of\ reactant} \times 100$$

$$Selectivity\ of\ product\ i\ (\%) = \frac{Moles\ of\ product\ i}{Total\ moles\ of\ product} \times 100$$

Results and Discussion

Toluene disproportionation reaction in plug flow reactor with powder, pellet and ZSM5 coated monoliths

The effect of washcoat thickness on the disproportionation of toluene in a monolith reactor was studied by varying the coating thicknesses of the monolith pieces used in the reaction. For

comparison, reaction runs were also carried out with ZSM5 pellets. All the runs were carried out at atmospheric pressure. The conversion versus temperature for the ZSM5 pellet and the monoliths with washcoat thickness between 10%-60% at a constant W/F_{Ao} (20 gcat h/mol) are plotted in Figure 1. The data suggests that the conversion is affected by diffusional resistances in the washcoat layer as the conversion progressively goes down with increase in washcoat thickness. For the pellet samples, lower toluene conversions were obtained primarily due to longer diffusion length inside the pellet and presence of binders.
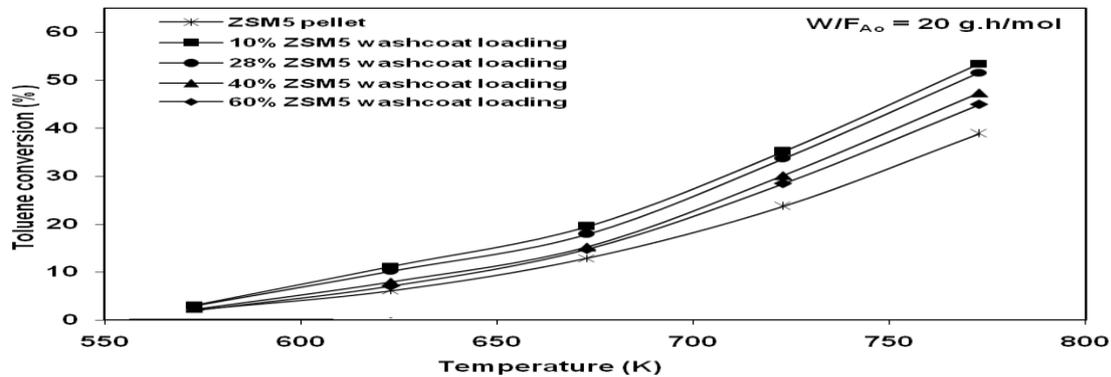
Figure 1: Effect of temperature and washcoat thickness on toluene conversion (W/F_{Ao} =20 gcat h/mol)
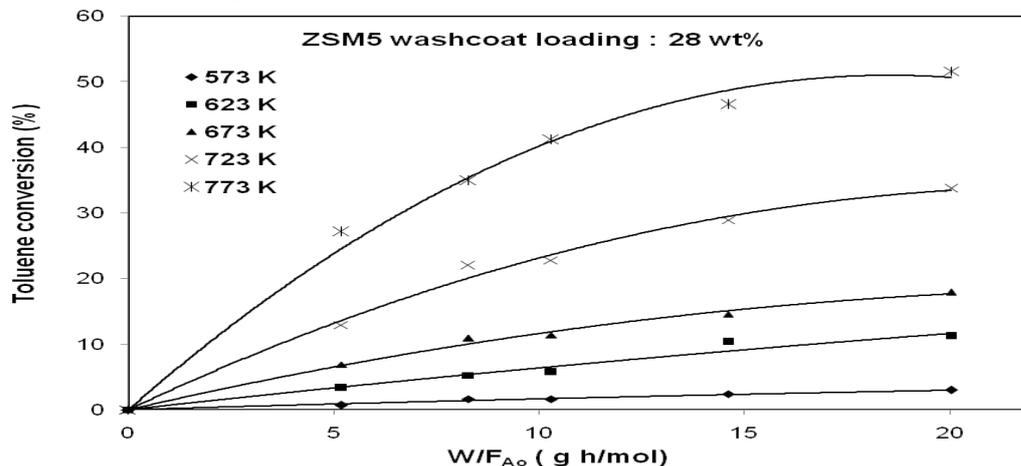
Figure 2: Toluene conversion as a function of temperature and W/F_{Ao} for 28% wascoated monolith.

Figure 2 shows the change in conversion with increase in W/F_{Ao} at different temperatures for 28% washcoat loading monolith. The conversion of toluene increased with temperature and W/F_{Ao} for both pellet (not shown in figure) and monolith catalysts. The disproportionation of toluene let to the formation of the following products: benzene, p-xylene, m-xylene, o-xylene, and gaseous hydrocarbons (methane, ethane, ethylene, and propylene) [11,12].

Table 1 shows the product distribution obtained by disproportionation of toluene at temperatures ranging between 573 and 773 K for washcoated monolths with 28% and 41% loading. The products indicate the presence of gaseous hydrocarbons in the effluent gases. This could be due to the secondary dealkylation reaction taking place along with disproportionation. The amount of gases increase with increase in temperature. The benzene to xylene ratio in product also shows values close to 1 and the ratio increases with temperature and space time. This implies that the presence of xylenes was required for larger amounts of gaseous hydrocarbons to be formed, as observed by previous workers.

Table 1. Product distribution for 28 wt% and 41 wt% washcoated monoliths at different temperatures (W/F_{Ao} =18 gcat h/mol)

Temperature, K	573		623		673		723		773	
Products	mol%		mol%		mol%		mol%		mol%	
Washcoat loading	28 wt%	41 wt%	28 wt%	41 wt%	28 wt%	41 wt%	28 wt%	41 wt%	28 wt%	41 wt%

Methane	0.11	0.25	0.05	0.28	0.07	0.41	0.07	0.52	0.21	0.56
Ethane	0.09	0.13	0.09	0.14	0.13	0.23	0.14	0.19	0.19	0.23
Ethylene	0.02	0.05	0.09	0.20	0.26	0.31	0.56	0.43	1.13	0.88
Propylene	0.86	0.84	1.36	0.95	1.83	1.06	1.93	1.75	3.02	2.04
Benzene	48.97	49.1	49.33	48.9	48.97	48.8	49.33	48.3	48.36	47.7
Ethylbenzene	0.14	0.06	0.22	0.08	0.17	0.18	0.16	0.26	0.18	0.28
p-xylene	18.24	18.28	13.97	15.11	12.75	13.5	12.26	12.2	11.29	11.8
m-xylene	24.36	25.37	25.78	24.4	25.73	25.3	24.59	24.3	24.08	24.5
o-xylene	6.67	5.61	8.81	9.14	9.69	9.05	10.28	10.7	10.28	10.2
C_{9+} compounds	0.54	0.33	0.30	0.82	0.39	1.05	0.59	1.41	0.59	1.85

The thermodynamic equilibrium concentration of xylene isomers are in the approximate ratio of para: meta: ortho = 1:2:1. The values given in Table 1 show that the para to meta and para to ortho isomer ratios are higher than those predicted by equilibrium. The presence of the catalyst in thin layers on the channels of the monoliths exposes more zeolite channel openings for reactant entrance and product exit, resulting in improved performance. Amongst the three isomers, p-xylene has the smallest molecular diameter and the configurational diffusivity of p-xylene is 1000 times greater than that of the meta and ortho isomers. Consequently, it can easily diffuse out of the ZSM5 pores as soon as it is formed and can exit the numerous exposed pores and diffuse into the bulk phase without further isomerization. However, as the thickness of the catalyst washcoat increases, the diffusional path length becomes longer, and transport resistances increase. This decrease in selectivity to p-xylene occurs because it has a greater chance of being reabsorbed and further isomerized.

Hydrogenation of 2-butyene-1, 4-diol in slurry and stirred tank reactors with monoliths:

In a stirred tank reactor, the monolith is typically placed in a basket or cage, which is suspended from a stirrer. The reactants are pumped into the reactor and mixed using the stirrer, which creates turbulence and promotes mass transfer between the fluid and the monolith. The reaction takes place on the surface of the monolith, and the products are then separated from the reaction mixture. Reaction studies were carried out with powdered Pd/ Al_2O_3 catalysts in a slurry reactor and in a stirred tank reactor fitted with Pd/ Al_2O_3 coated cordierite monoliths. The hydrogenation of 2-butyne-1,4 diol (A) to form 2-butene-1, 4 diol (B) is a series reaction. 2-butene-1, 4 diol further reacts to form butane-1,4 diol (C), n-butanol (D), and 2-hydroxytrtrahydrofuran (E). The effect of the reaction temperature on the initial reaction rate of A to B was studied in the range of 323-333 K at a H_2 pressure of 3 atm and with an initial reactant concentration (C_{A0}) of 30 g/l. Runs are taken with 2 g of powder catalysts containing 0.5% Pd. The variation of (C_A/C_{A0}) with the reaction run time at different temperatures is shown in Figure 3.
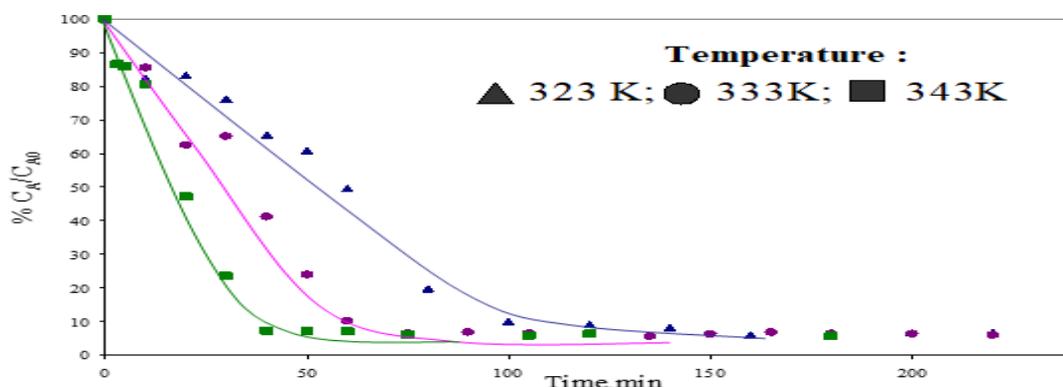
Figure 3: Percentage of C_A/C_{A0} vs. runtime at different temperatures (initial reactant concentration 30 g/l; H_2 Pressure= 3 atm)

The initial reaction rate at different temperatures were calculated from the initial slope of these curves and they are been represented in Figure 4 with a variation of temperatures.
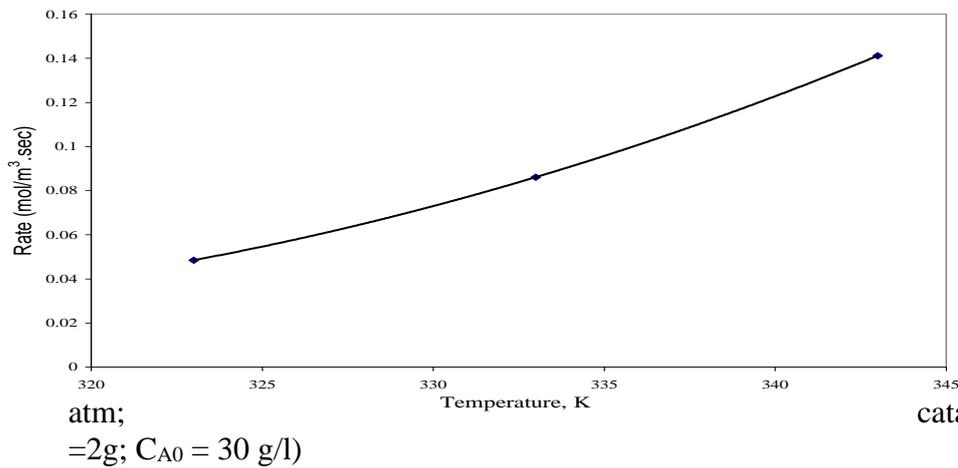
Figure 4: Initial rates at different temperatures (stirring speed = 400 rpm; H$_2$ Pressure= 3 atm; catalyst weight =2g; C$_{A0}$ = 30 g/l)

In the monolithic stirred tank reactor, the runs are taken to investigate the effect of washcoat thickness on the initial rate of reaction as well as the product selectivity. Based on the previous studies on the washcoat, it observed that with increase in alumina loading, the thickness of the monolithic washcoat increased uniformly to the monolithic channels, upto an alumina loading of 60%. That was confirmed with the help of SEM images of the washcoated monoliths. Therefore, the range of alumina loading considered for the study is restricted upto an alumina loading of 60%.

The runs were taken at a temperature of 60°C and a H$_2$ pressure of 3 atm with C$_{Ao}$ of 15 g/l. The variation of C$_a$/C$_{Ao}$ with reaction time is shown in Figure 5.
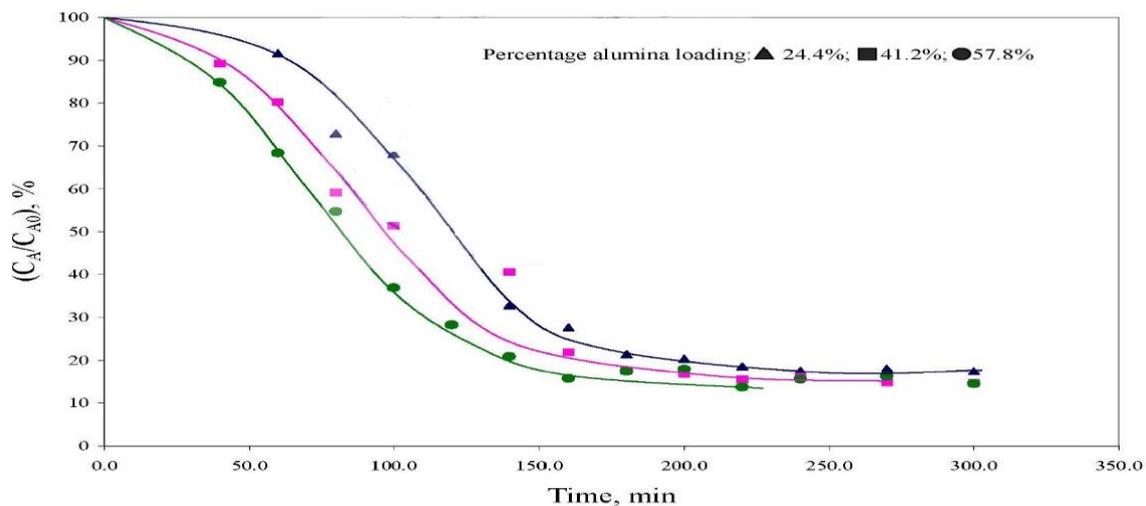
Figure 5: Variation of C$_A$/C$_{Ao}$ with time using Pd/Al$_2$O$_3$ loaded monoliths
(H$_2$ Pressure= 3 atm;   Temperature =333 K; C$_{A0}$ = 15 g/l)

The selectivity to B for these runs is shown in Figure 6. This plot shows that selectivity to B was higher when the washcoat thickness was more. It is well known that for consecutive reactions, the intermediate product is favoured when the catalyst diffusional resistances are lower. These trends confirm that diffusional resistances were affected both the activity and selectivity to B for the monolithic catalysts. Figure 7 shows the selectivity of C and D with variation in reaction time. The selectivity to C decreased whereas the selectivity to D increased with an increase in alumina loading. Selectivity to E was not appreciably affected by an increase in washcoat thickness.

Figure 6: Selectivity of B with time using Pd/Al$_2$O$_3$ loaded monoliths (H$_2$ Pressure= 3 atm; Temperature =333 K; C$_{A0}$ = 15 g/l)

Figure 7: Selectivity of C and D with time using Pd/Al$_2$O$_3$ loaded monoliths
(H$_2$ Pressure= 3 atm;   Temperature =333 K; C$_{A0}$ = 15 g/l)

Conclusion

Monolith reactors can be successfully used for both plug flow as well as stirred tank reactors.
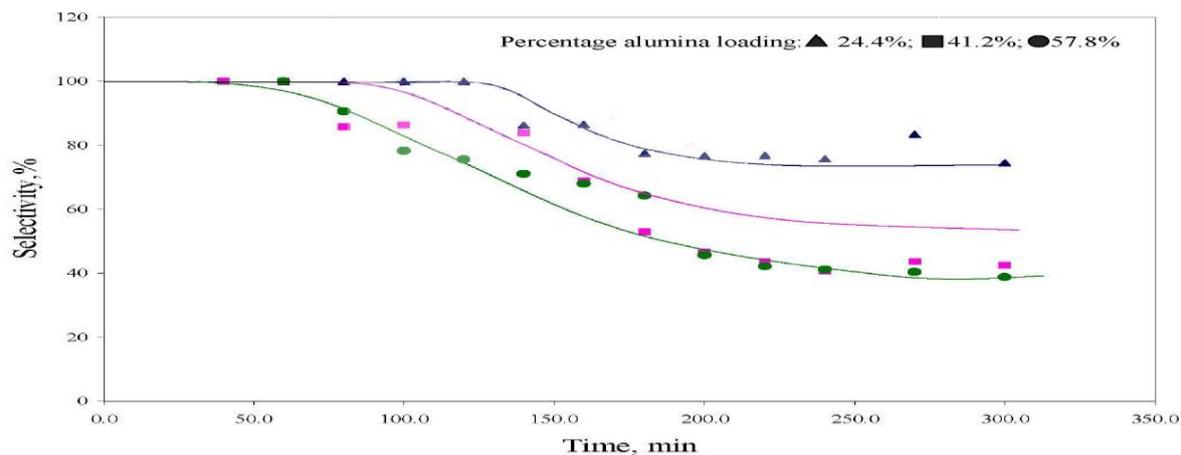
For the plug flow configuration, Monoliths coated with ZSM5 and loaded between 10 to 60 wt% exhibit activity for the toluene disproportionation reaction. The conversion of toluene is
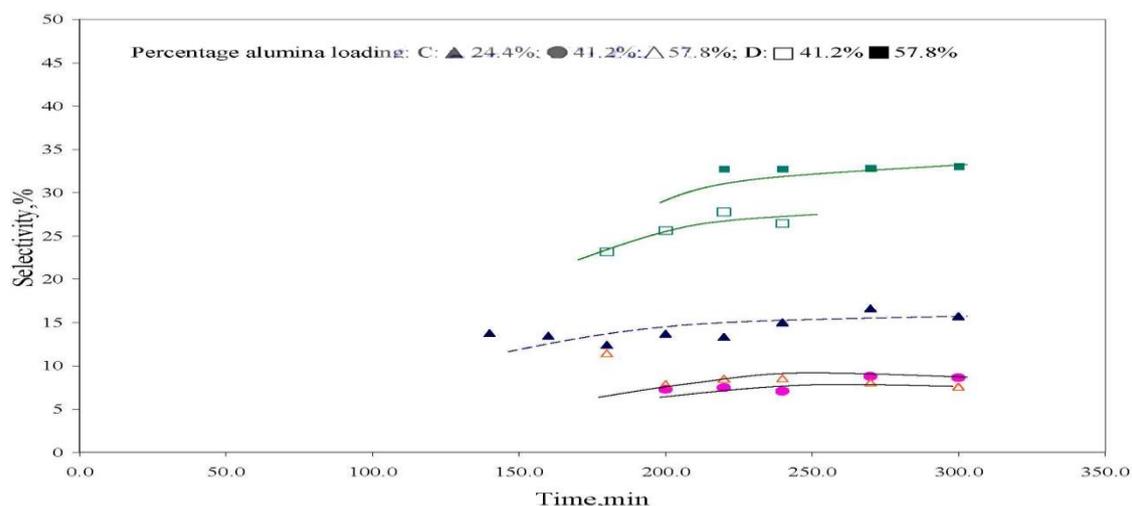
improved with increasing temperature and W/F_{Ao}, which is similar to the behavior of ZSM5 powder catalysts. However, when the thickness of the washcoat is increased, the conversion is decreased because of the enhancement of internal diffusional limitations. The products (benzene, xylene isomers, and gaseous hydrocarbons) of the toluene disproportionation reaction on washcoated monoliths is similar to that obtained from packed bed reactors using powder or pellet catalysts. The selectivity of the monolith catalysts for p-xylene is higher than the equilibrium value. The p-xylene selectivity is a function of temperature and thickness of the washcoat. The p-xylene that is initially formed during the disproportionation reaction can easily diffuse out of the zeolite pores in the thin washcoats and move into the bulk phase. This prevents further isomerization of p-xylene to the other isomers leading to high p-xylene selectivity.

For the stirred tank reactor, the rate of hydrogenation of 2-butyene-1, 4-diol decreased with an increase in alumina washcoat thickness of the monoliths, due to an increase of the diffusional limitation to the catalyst pores. The desired intermediate product, obtained in the hydrogenation of 2-butyene-1, 4-diol (A), is 2-butene-1, 4-diol (B). This undergoes further hydrogenation to butane-1, 4-diol (C). Other side products of the reaction are n-butanol (D) and 2-hydroxytetrahydrofuran (E). The selectivity to all these products is also affected with the change in washcoat thickness.

References

[1] Cybulski A, Moulijn JA, eds. *Structured Catalysts and Reactors*. New York: Marcel Dekker Inc, 1998.

[2] Heck RM, Gulati S, Farrauto RJ. The application of monoliths for gas phase catalytic reactions. *Chem. Eng. J.* 2001; 82: 149-156.

[3] S. Roy, A. K. Heibel, W. Liu and T. Boger, *Design of monolithic catalysts for multiphase reactions*, Chemical Engineering Science, 2004, 59, 957-966

[4] M.E. Davis, *Zeolite-based catalysts for chemicals synthesis*, Microporous and Mesoporous Materials, 1998, 21,173-182

[5] R.E. Albers, M. Nystrom, M. Siverstrom, A. Sellin, A.C. Dellve, U. Andersson, H. Herrmann and T. Berglin, 'Development of Monolith Based Process for H_2O_2 Production: From Idea to Large-Scale Implementation', Catal. Today, **69**, 247 (2001)

[6] Beltrame P, Beltrame PL, Carniti P, Forni L, Zuretti G. Toluene disproportionation catalysed by various zeolites. *Zeolites.* 1985; 5: 400-405.

[7] J. M .Winterbottom,H, Marwan, J. Viladevall, S. Sharma, S. raymahasay, Heterogeneous catalysis and fine chemicals IV in : H.V. Blaser, A. Baiker, R. Prins (Eds) ,Stud.Surf.Sci.Catal.108(1997)59

[8] R.V. Chaudhari, in: R.V. Chaudhari, H. Hofmann (Eds.), in: Proceedings of the Indo–German Workshop on High Pressure Technology — Engineering, Forschungszentrum Julich GmbH, 1993, p. 197

[9] B. Mitra, J. P. Chakraborty, D. Kunzru, Disproportionation of toluene on zeolite washcoated monoliths, AIChE Journal 57 (2011) 3480-3495.

[10] D. Chatterjee, M. Tech thesis, 2007

[11] Young LB, Butter SA, Keading WW. Shape-selective reactions with zeolite catalysts III. Selectivity in xylene isomerization, toluene-methanol alkylation, and toluene disproportionation over ZSM-5 zeolite catalysts. *J.Catal*. 1982; 76: 418-432.

[12] Meshram NR, Hedge SG, Kulkarni SB, Ratnasamy P. Disproportionation of toluene over HZSM-5 zeolites. *Appl.Catal.* 1983; 8: 359-367.