AIChE WILEY InterScience® DISCOVER SOMETHING GREAT

α-Methylstyrene Hydrogenation in a Flow-Through Membrane Reactor

H. Purnama, P. Kurr, A. Schmidt, and R. Schomäcker
Technische Universität Berlin, Institut für Chemie, D-10623 Berlin, Germany

I. Voigt
Hermsdorfer Institut für Technische Keramik eV, 07629 Hermsdorf-Thüringen, Germany

A. Wolf and R. Warsitz
Bayer Technology Services GmbH, 51368 Leverkusen, Germany

DOI 10.1002/aic.10893

The hydrogenation of α-methylstyrene (AMS) was carried out in a flow-through membrane reactor at: 45–50°C, 1–40 bar, and 18 vol % AMS in heptane. An α-Al_2O_3 membrane tube of defined pore size was used as catalyst support material. A wet impregnation method was used to prepare the active membrane with palladium as catalyst. Experiments with a spherical Pd/Al_2O_3 egg-shell catalyst in a slurry reactor were carried out under similar reaction conditions for comparison. Results from the flow-through membrane reactor were also compared to results from other types of reactors described in the literature. Application of the flow-through membrane reactor exhibits an enhanced performance with respect to the productivity (reaction rate per mass of palladium) relative to that of other types of membrane reactors and other conventional reactors, such as a slurry reactor, a trickle-bed reactor, and a bubble-column reactor.

Keywords: hydrogenation of α-methylstyrene, flow-through membrane reactor, slurry reactor, palladium catalyst, activity

Introduction

The hydrogenation of α-methylstyrene (AMS) to cumene over a Pd catalyst supported on an α-Al_2O_3 membrane was chosen as a model reaction for three-phase reaction to study mass transfer effects on the reaction rate.[1-7] Detailed microkinetic analyses of this reaction were previously reported in the literature.[8-10] Studies of such three-phase reaction systems (solid–gas–liquid) focusing on the reactor design have been discussed in a variety of publications.[6,11-13] The hydrogenation of AMS to cumene has been found to be an excellent test reaction because of its mild exotherm ($\Delta H_R = -109$ kJ/mol), nonvolatile reactant and product, and the expected simplicity of the reaction (according to Meille et al.[10] AMS is converted exclusively to cumene by the palladium catalyst). The study of Pd-catalyzed hydrogenation of AMS has been carried out in numerous types of reactors, such as trickle-bed reactors,[2,5-7,14-17] slurry reactors,[3,8,10,18] bubble-column reactors,[13] monolith reactors,[1,4,19] and membrane reactors.[12,20] Generally, the main problems of three-phase reactions of this kind are the low solubility of hydrogen in the liquid phase and the mass transfer limitation.

To achieve efficient use of the expensive Pd catalyst and also to overcome the mass transfer limitation, several new concepts based on membrane reactors have been studied. The advantages of using the membrane reactor are (1) no need of liquid–

Correspondence concerning this article should be addressed to R. Schomäcker at Schomaecker@tu-berlin.de.

solid separation, (2) enhanced mass transfer, and (3) the absence of hotspots. With these features it is especially suitable for highly exothermic reactions.[21] A new concept for hydrogenation of AMS in a membrane reactor with a porous composite membrane from Ni ($>$70%) has been reported by Kuzin et al.[12] To minimize the mass transfer limitations, the hydrogenation of AMS was performed in the reactive evaporation mode (gas phase). This means that the reaction mixture is a two-phase system, that is, a solid–gas reaction. The contact between the evaporated reactants, the catalyst, and hydrogen occurs within the membrane. The authors assumed that the amount of heat required for the evaporation could be provided by the reaction itself.

The preparation of the active membrane in the form of a hollow tube is based on the methods of powder metallurgy. With respect to the application of nickel catalysts in the hydrogenation of AMS, it must be considered that nickel catalysts can also catalyze the polymerization of AMS and that the reaction rate is significantly lower than that using a Pd catalyst. The required content of palladium as an efficient catalyst for hydrogenation of AMS was found to be $<$1 wt %. However, external cooling is required to separate the hydrogen and the liquid (unconverted AMS and cumene) in the product stream. By the application of this membrane reactor, limitations arising from liquid-phase transport can be neglected.

The objective of this work is to study the activity of palladium deposited in a flow-through membrane reactor compared to conventional reactors. A hollow, microporous alumina tube with a pore diameter of 1.9 μm was used as catalyst support material. The palladium metal was loaded onto the porous membrane by a wet impregnation method. Before introducing the reactant (AMS diluted in heptane or cumene) into the membrane, it is saturated with hydrogen in a vessel. To obtain a high conversion, the reactant solution is resaturated and recirculated through the membrane. Given the convective flow of the reactant through the membrane, diffusion mass transfer limitations may be neglected. An improvement in the efficient use of the palladium metal that serves as catalyst is reported.

Experimental

Membrane impregnation

The tubular membrane made of microporous α-Al_2O_3 has an average pore diameter of 1.9 μm, a wall thickness of 1.0 mm, an external diameter of 2.9 mm, and a length of 250 mm. The impregnation is done by soaking the tubes for 24, 48, 72, and 96 h with an saturated organic solution of palladium acetate (10.8 g/L in toluene) at ambient temperature. The tubes are dried at room temperature for 24 h and reduced in a flow of hydrogen gas at 70°C for 2 h.

Determination of the palladium mass

To determine the mass of palladium deposited in the membrane, the impregnated membrane tube was soaked in 5 mL aqua regia for 24 h. A 1-mL sample of the solution was removed and diluted with water to 50 mL. The concentration of the palladium in the solution was determined by atomic absorption spectroscopy (AAS).

Setup and procedures

Measurements of the hydrogenation of AMS were performed in a reactor system as shown in Figure 1 at different pressures between 1 and 40 bar. The membrane reactor (a stainless steel filtration module) was placed in an aluminum heating block for improved heat transfer. Six cartridge heaters of 75 W each were placed inside the aluminum block. The temperature of the reactor was controlled by PID (proportional integrative derivative) control of the cartridge heaters. Three type J thermocouples [Fe vs. (Cu + 43%Ni)] were used to monitor the temperature. One was placed in the aluminum block; the other two were placed one each at the inlet and outlet of the membrane module. Before the activity measurements, the tubular ceramic catalytic membrane was activated under hydrogen flow at 70°C for 2 h. The reactant (AMS) and the solvents (*n*-heptane, methylcyclohexane, and cumene) were used as received from Aldrich. Before starting the hydrogenation, the reaction mixture (20 mL AMS and 90 mL *n*-heptane) was loaded into a stainless steel vessel that served as a saturation vessel. This vessel was equipped with a gas-inducing turbine and baffles. Under hydrogen pressure and a stirrer speed of 1600 rpm, the mixture was heated to the desired temperature of 50°C (thermostat-controlled). The reaction is started when the liquid is introduced into the membrane module by a pump. Because the conversion of AMS to cumene per passage is low, the reactor is operated in a recycle mode. The range of the volumetric flow rate within the circuit was varied from 50 to 500 mL min^{-1}. The hydrogen pressure in the saturation vessel is kept constant during the reaction. After initiation of the reaction, small amounts of the mixture were removed every 5 min from the reactor outlet for product analysis. The composition was analyzed using gas chromatography. For slurry experiments with powder catalyst, the saturation vessel was used as a reactor. The slurry experimental conditions were similar to those described for the membrane reactor measurements. Two types of commercial palladium catalyst supported on α-Al_2O_3 spheres were used in the experiments. One of the catalysts was the egg-shell catalyst and the other was a porous catalyst (Pd distributed uniformly in the porous support material). The loading for both catalysts was approximately 0.5 wt % based on the Al_2O_3 mass.

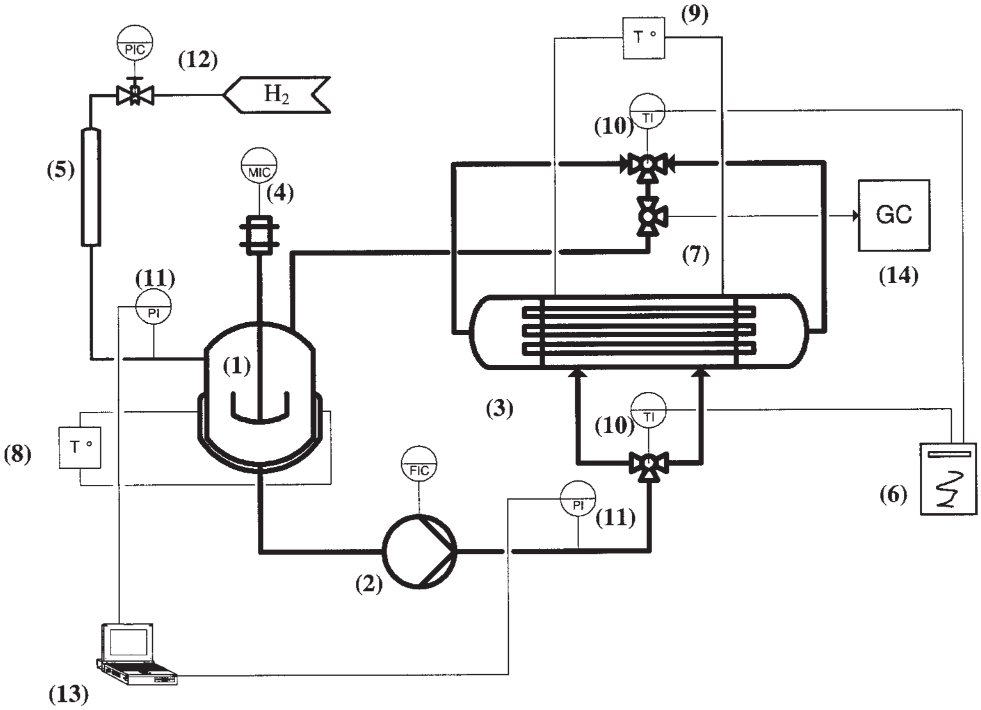
Results and Discussion

Impregnation of the membrane

The amount of the impregnated Pd was in the range from 0.8 to 2.4 mg (0.03–0.08 wt %). Broad distributions (20%) of the experimental results were observed for the same time of impregnation. Furthermore, there is no correlation between the period of the impregnation and the amount of the Pd deposited on the membrane. The Pd was mainly deposited as particles on the pore walls of the membrane with a layer of about 200 μm below the pore mouth.

Slurry reactor

The reaction rate that also indicates the productivity is described by the following equation:



1. Saturation vessel
2. Pump
3. Membrane reactor
4. Stirrer
5. Hydrogen reservoir cylinder
6. Temperature plotter
7. Sample outlet
8. Thermostat
9. PID-controller
10. Thermocouple
11. Pressure transformer
12. Hydrogen blocking valve
13. Computer for monitoring the pressure
14. Gas chromatograph

Figure 1. Experimental setup of flow-through membrane reactor with saturation vessel.

$$r = \frac{1}{m_{\mathrm{Pd}}}\left(\frac{dn_{\mathrm{AMS}}}{dt}\right)$$

where r is the overall reaction rate, m_{Pd} is the mass of the active component (Pd), and dn_{AMS} is the consumption of AMS during the time interval dt; r is expressed with the unit of μmol g_{Pd}^{-1} s^{-1} for all the experimental results reported in this work. First, the reaction rate was studied as a function of stirring speed in the saturation vessel from 800 to 1600 rpm. The observed influence of stirring speed on the reaction rate indicates the presence of mass transfer limitations. Stirring speeds of $>$1600 rpm show no further increase in reaction rate, indicating experiments free of gas–liquid mass transfer limitation. The gas–liquid volumetric mass-transfer coefficient ($k_L a$) was determined experimentally under the following operating conditions: 25°C, stirring speed of 1600 rpm, 100 mL *n*-heptane, and pressures of 20 and 40 bar, respectively. The value of $k_L a$ was found to be 0.15 s^{-1} for both pressures. Similar experimental results were reported by Meille et al.[10]

A study of mass transfer limitations caused by intraparticle diffusion in the porous catalysts was also carried out. To provide a database for benchmarking of the performance of the catalytic membrane reactor, two different types of catalysts—egg-shell and porous full catalysts—were studied. Each of these catalysts was measured in two different particle sizes, as spheres with a diameter of about 3 mm (as received) and as powder (about 100 μm), obtained by crushing the sphere. Both the egg-shell catalyst in the form of spheres and the powder display higher activity than that of the porous full catalyst, as can be seen in Figure 2. The powdered egg-shell catalyst shows somewhat better activity compared to that of the spherical one. Considering the same mass of catalyst or active component, it

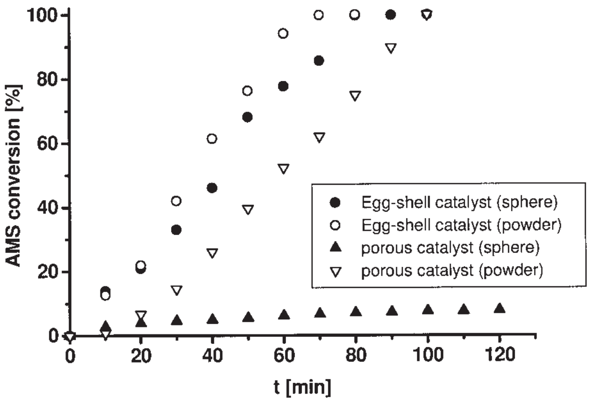


Figure 2. Investigation of the internal mass transfer limitation on different forms of catalysts in slurry reactor.

Reaction conditions: 40 bar, 53°C, 0.86 g catalyst, 18 vol % AMS in heptane.

would be expected that the activity of the egg-shell and porous catalyst (both in the form of a powder) would be about the same, although this is not the case. The results show that pore diffusion limitation is still present with the powdered porous catalyst, indicating that the small particles obtained by crushing the spheres are not small enough to exclude pore diffusion limitation. Because of the strong mass transfer limitation in the porous catalyst spheres, this catalyst shows the lowest activity. As expected, the powdered egg-shell catalyst provides the highest activity (4000 μmol s^{-1} $g_{Pd}{}^{-1}$) as a result of the lowest resistance to mass transfer limitation by pore diffusion. The activity of the powdered porous full catalyst is 20% lower than the activity of the powdered egg-shell catalyst. The pellets of the porous full catalyst show the worst activity (250 μmol s^{-1} $g_{Pd}{}^{-1}$). The effectiveness factor of this catalyst is estimated to be about 0.05 for this reaction. The effectiveness factor for the spherical egg-shell catalyst, on the other hand, is 0.8. The reaction rate is found to be independent of the initial concentration of AMS. As reported in the literature,[10] the hydrogenation of AMS is a zero-order reaction with respect to AMS and first-order with respect to hydrogen. This correlates well with our results.

The catalyst stability studies were carried out in a slurry reactor as shown in Figure 3. The activity of the catalyst decreases within the series of three experiments. It is assumed that catalyst deactivation results from the polymerization of trace AMS and adsorption of the polymer on the active surface of the catalyst. Furthermore the shapes of the curves of these three measurements are observed to be different. In the first run, the conversion increased almost linearly with time. In the second and third runs, a sigmoidal curve is observed. The shape of the S-form becomes more pronounced with the number of experimental runs, which could indicate that a removal of side products deposited on the catalyst surface takes place before the catalyst starts to work again. A study of the mass transfer limitations in hydrogenation of AMS in monolith reactors was reported by Kreutzer et al.[1] A deactivation of the catalyst was also observed in their experiments. To minimize the deactivation, high hydrogen pressures were maintained during the cooling down of the reactor. Unfortunately, reasons for the deactivation were not reported in this or other references.

Flow-through membrane reactor

To study the influence of the geometry of the membrane reactor, the reaction mixture was fed across the membrane in two modes: from the outside to the inside of the membrane tube and vice versa. The results for the AMS conversion show that the flow direction has no significant influence on the reaction rate. The rate of the AMS hydrogenation in the flow-through membrane reactor is determined by the palladium content of the membrane (Figure 4). The correlation between the activity (μmol s^{-1} L^{-1}) and the Pd content is not linear, as shown in Figure 4b, because the surface area of the Pd is responsible for the activity. The nonlinear correlation between activity and mass of Pd is caused by the nonlinear increase of Pd surface with mass of Pd deposited.

In Figure 5, the overall reaction rate is shown as a function of the flow rate of the recycled reaction mixture. The overall reaction rate increases with increasing flow rate. For higher flow rates (from 450 mL/min) the curve levels off slightly. This correlation between the overall reaction rate and the flow rate is a consequence of the hydrogen supply of the catalyst. To the extent that the overall reaction rate is a function of flow rate, this means that part of the Pd catalyst that is deposited on the membrane is not used in a highly efficient way. Therefore the optimum utilization of Pd catalyst in the membrane reactor can be obtained by adjusting the flow rate or the amount of Pd on the membrane.

For a comparison of different reactor types, such as membrane and slurry reactors, similar reaction conditions were chosen. The mass of palladium used in the slurry experiment was 4.3 mg and in the membrane reactor, 1.3 mg. Although the amount of Pd in the membrane reactor is significantly lower than that in the slurry reactor, the result reveals that the reaction rate in the membrane reactor is higher than that in the slurry reactor for all pressures investigated here. In the slurry experiments, the overall reaction rate increases linearly with increasing hydrogen pressure. On the other hand, a disproportionate increase of the overall reaction rate with hydrogen pressure is observed in the membrane reactor. The catalyst used in the

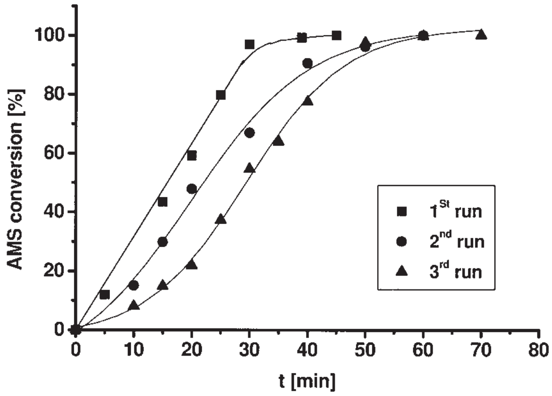


Figure 3. Stability measurement of the palladium egg-shell catalyst in slurry reactor.

Reaction conditions: 10 bar, 53°C, 0.86 g catalyst, 50 vol % AMS in cumene.

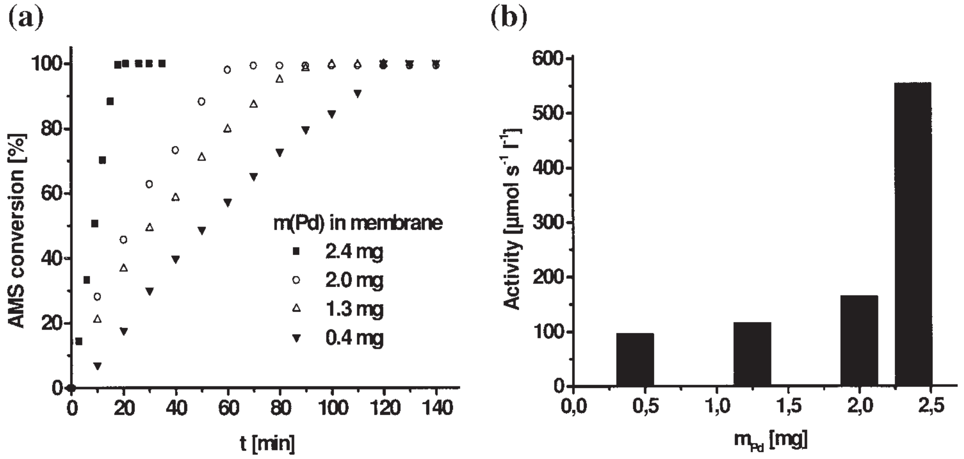


Figure 4. (a) and (b) Conversion rate and activity as a function of Pd content in membrane reactor.

Reaction conditions: T = 38 °C, $p(H_2)$ = 1 bar, 0.7 mol L^{-1} AMS in cumene, 1600 rpm, membrane pore size: 1.9 μm, flow rate 490 mL/min.

slurry reactor was the egg-shell catalyst in the form of spheres. The rate enhancement in the membrane reactor compared to that in the slurry reactor is caused by the more efficient use of Pd with increasing hydrogen pressure. There are two possible explanations for this observation. First, because of the convective flow of the liquid reactant across the membrane almost all of the Pd catalyst is accessible to the reactants. Second, the particle size of the palladium supported on the ceramic membrane is significantly smaller than that of the egg-shell catalyst as indicated by SEM.

An investigation of the Pd surface area by using CO absorption for both the egg-shell catalyst and the ceramic membrane is one of our next objectives. Concerning the study of the hydrogenation of AMS in different types of reactors, a selection of results from the literature is compared to the results from this study in Figure 6. Comparison of the reactors is based on the overall reaction rate at comparable reaction conditions: 50°C reaction temperature and 1 bar hydrogen pressure. However, for a comparison of different reactor types compromises always have to be found because there are differences in catalyst geometry, Pd loading, and Pd particle size. For example, the membrane studied by Cini et al.[20] is not comparable to the membrane in this work. It is a hollow, macroporous α-Al_2O_3 tube that is coated on its inside wall with a thin layer of Pd-impregnated microporous γ-Al_2O_3. The liquid flows outside of the tube, whereas the gas flows inside of the tube. The Pd loading of 1.8–2.5 wt % is higher than that in our work. The Pd loadings of the catalysts in the trickle-bed reactors[6,7,17] range from 0.5 to 2.5 wt %. From this survey of catalyst and reactor systems the results from the membrane reactor as well as the slurry reactor used in this study generally show higher overall reaction rates compared to that of all other types of reactors. One exception is the overall reaction rate calculated from the intrinsic kinetics studied by Meille et al.[10] The main reason for the discrepancy between our result and that reported by Meille is the different particle sizes of catalyst used in the investigations: the particle size of the catalyst used by Meille was 10 μm in contrast to 100 μm in our experiments. This difference in particle size already

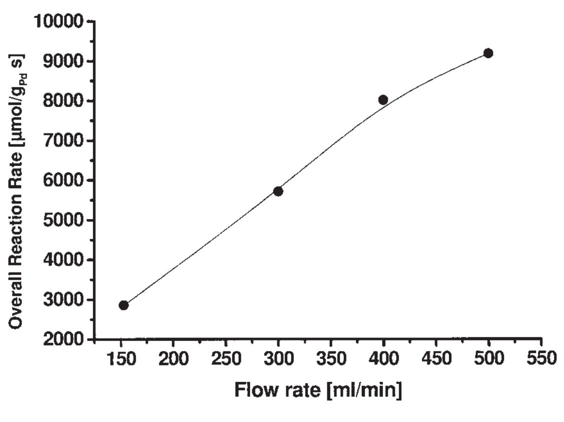


Figure 5. Overall reaction rate as a function of flow rate in membrane reactor.

Reaction conditions: 40°C, 1 bar, 1600 rpm, 0.35 mol L^{-1} AMS in heptane, membrane pore size = 1.9 μm, m_{Pd} = 2.1 mg.

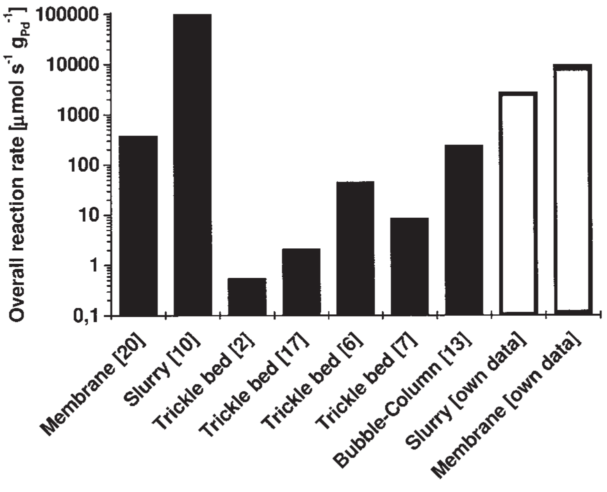


Figure 6. Comparison of the overall reaction rate per gram Pd for the AMS hydrogenation in different types of reactors.

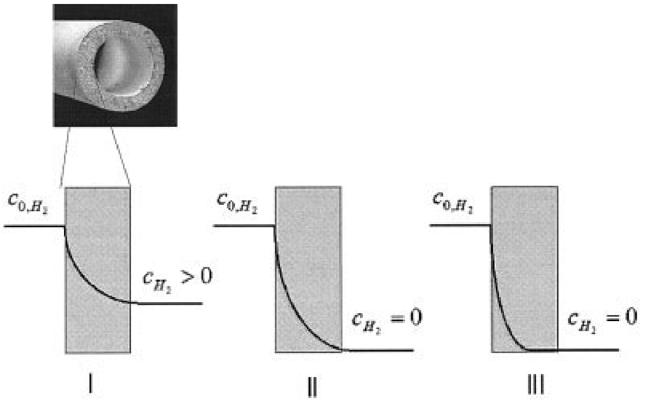


Figure 7. Conversion of hydrogen within the Pd/Al_2O_3 membrane at different flow rates.

$FR_I > FR_{II} > FR_{III}$.

causes some mass transfer limitation in the catalyst pore of the bigger particles. Only in particles of $\leq 10\ \mu m$ is no mass transfer limitation observed.[10] Nevertheless, apart from the productivity obtained from the study of the intrinsic kinetics in the slurry reactor, the flow-through membrane reactor in our study shows the highest productivity compared to that of conventional reactors such as slurry, trickle bed, and bubble-column reactors. Considering the powder catalyst, it has to be kept in mind that such fine powder catalysts never find application in technical scale because of the difficulty of separating them from the product. The studies carried out by Meille and coworkers aimed exclusively at determination of kinetic data.

Conclusions

The hydrogenation of AMS was studied in a flow-through membrane reactor and compared to (1) results of slurry experiments carried out in parallel and (2) results from different reactors reported in the literature. The objective of the comparison is the overall reaction rate (productivity), defined as the conversion of AMS per time and per mass of palladium. The flow-through membrane reactor exhibits a higher productivity than that of slurry, trickle-bed, bubble-column, and diffusor membrane reactors, which is attributed to the more efficient utilization of the palladium catalyst when it is deposited on a membrane. This means that the contact area between the liquid and the solid can be enhanced. An additional reason concerning the higher productivity of the flow-through membrane reactor compared to that of standard reactors reported in Figure 6 is the higher dispersion of palladium particles on the membrane. It has been found in this study that the flow rate of the reactants through the membrane clearly plays an important role for the performance of a flow-through membrane reactor. Adjustment to an adequate flow rate will provide a highly efficient utilization of the palladium catalyst supported in the ceramic membrane.

For a discussion of the observed behaviors, three situations may be distinguished. Figure 7 shows the consumption of hydrogen within the membrane. For the first case, the flow rate of the reactants through the membrane is highest so that the hydrogen is not completely converted within the membrane. The overall reaction rate in this case is higher than that in cases II and III where a slow flow rate causes a strong decrease of hydrogen concentration within the membrane. The optimal condition applied in the system is described in case II. The hydrogen is completely converted when the reactant leaves the membrane. In the third case, the residence time (adjusted by the flow rate) of the reactants within the membrane is in a range in which the hydrogen concentration already reaches zero within the membrane. As a result, part of the Pd catalyst in the membrane remains unused. Comparison of the three situations shows that both the Pd content of the membrane and the flow rate of the reactants must be carefully adjusted for optimal utilization of the catalytically active membrane. Further application of this flow-through membrane reactor will focus on its catalytic performance in partial hydrogenation reactions of multiply unsaturated components.

Acknowledgments

This work was supported by the Federal Ministry for Education and Research (BmBF), Germany.

Literature Cited

1. Kreutzer MT, Du P, Heizwolf JJ, Kapteijn F, Moulijn JA. Mass transfer characteristics of three-phase monolith reactors. *Chem Eng Sci.* 2001;56:6015-6023.
2. Turek F, Lange R. Mass transfer in trickle-bed reactors at low Reynolds number. *Chem Eng Sci.* 1981;36:569-579.
3. Johnson DL, Saito H, Polejes JD, Hougen OA. Effects of bubbling and stirring on mass transfer coefficients in liquids. *AIChE J.* 1957;3:411-417.
4. Heizwolf JJ, Engelvaart LB, van den Eijnden MG, Kreutzer MT, Kapteijn F, Moulijn JA. Hydrodynamic aspects of the monolith loop reactor. *Chem Eng Sci.* 2001;56:805-812.
5. Beaudry EG, Dudukovic MP, Mills PL. Trickle-bed reactors: Liquid diffusional effects in a gas limited reaction. *AIChE J.* 1987;33:1435-1447.
6. Wu Y, Khadilkar MR, Al-Dahhan MH, Dudukovic MP. Comparison of upflow and downflow two-phase flow packed-bed reactors with and without fines: Experimental observations. *Ind Eng Chem Res.* 1996;35:397-405.
7. Satterfield CN, Pelossof AA, Sherwood TK. Mass transfer limitations in a trickle-bed reactor. *AIChE J.* 1969;15:226-234.
8. Ahn B, McCoy BJ, Smith JM. Separation of adsorption and surface reaction rates: Dynamic studies in a catalytic slurry reactor. *AIChE J.* 1985;31:541-550.
9. Chen S, McCoy BJ, Smith JM. Dynamic studies of catalyst poisoning: Effect of adsorption and surface reaction rates for hydrogenation of α-methystyrene by Pd/Al_2O_3. *AIChE J.* 1986;32:2056-2068.
10. Meille V, de Bellefon C, Schweich D. Kinetics of α-methylstyrene hydrogenation on Pd/Al_2O_3. *Ind Eng Chem Res.* 2002;41:1711-1715.
11. Turek F, Oertel R, Lange R. Zur Modellierung katalytischer Dreiphasenprozesse. *Chem Tech.* 1975;27:662-670.
12. Kuzin NA, Kulikov AV, Shigarov AB, Kirillov VA. A new reactor concept for hydrocarbon hydrogenation in the reactive evaporation mode. *Catal Today.* 2003;79:105-111.
13. Sherwood T, Farkas EJ. Studies of a slurry reactor. *Chem Eng Sci.* 1966;21:573-582.
14. Khadilkar MR, Al-Dahhan MH, Dudukovic MP. Parametric study of unsteady-state modulation in trickle-bed reactors. *Chem Eng Sci.* 1999;54:2585-2595.
15. Khadilkar MR, Wu YX, Al-Dahhan MH, Dudukovic MP, Colakyan M. Comparison of trickle-bed and upflow reactor performance at high pressure: Model predictions and experimental observations. *Chem Eng Sci.* 1996;51:2139-2148.
16. Turco F, Hudgins RR, Silveston PL, Sicardi S, Manna L, Banchero M.

Investigation of periodic operation of a trickle-bed reactor. *Chem Eng Sci.* 2001;56:1429-1434.
17. Turek F, Lange R, Rusch A, Löwe R. Experimental investigations of the hydrogenation of α-methylstyrene in a trickle-bed reactor. *Chem Tech.* 1975;27:149-152.
18. Ahn B, Smith JM, McCoy BJ. Dynamic hydrogenation studies in catalytic slurry reactor. *AIChE J.* 1986;32:566-574.
19. Nijhuis TA, Kreutzer MT, Romijn ACJ, Kapteijn F, Moulijn JA. Monolithic catalysts as efficient three-phase reactors. *Chem Eng Sci.* 2001;56:823-829.
20. Cini P, Harold MP. Experimental studies of the tubular multiphase catalyst. *AIChE J.* 1991;37:997-1008.
21. Watson PC, Harold MP. Dynamic effects of evaporation with exothermic reaction in a porous catalytic pellet. *AIChE J.* 1993;39:989-1006.

Manuscript received Oct. 5, 2005, and revision received Apr. 7, 2006.