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Catalysis Today 104 (2005) 305–312

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Selectivity of partial hydrogenation reactions performed in a pore-through-flow catalytic membrane reactor

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Abstract

The selectivity of partial hydrogenation reactions of unsaturated substrates was studied in a membrane reactor operating at 323 K and 40 bar hydrogen pressure. The reactor system was constructed as a loop of a saturation vessel and a membrane module in which the reaction mixture was resaturated with hydrogen up to 100 times. In a porous membrane made from cross-linked polyacrylic acid palladium nanoparticles were incorporated as catalysts. A well-defined residence time within the membrane was achieved due to a defined pore structure of the membrane and a convective mass flow of the reaction mixture through the membrane. The selectivity for the partially hydrogenated products was investigated as a function of the pore size of the PAA membrane and was compared to commercially available catalysts. Compared to experiments with supported catalysts (Pd/C and Pd/Al_2O_3) in a slurry and a fixed bed reactor the selectivity for the desired products could be increased by 3% (1-octyne) up to 40% (geraniol).

Keywords: Catalytic membrane reactor; Nanoparticles; Selectivity

1. Introduction

Hydrogenation reactions are of great industrial importance. Often they are a sequence of consecutive reactions where the desired product is the intermediate. An important aim is to receive the intermediate product selectively with a high conversion of the substrate. Fixed bed reactors packed with catalyst pellets are most frequently used for heterogeneously catalyzed hydrogenations [1]. A limiting factor here often is mass transport between the fluid and the gas phase as well as interparticular transport processes. Both effects decrease the selectivity for the desired products. A promising alternative are catalytic membrane reactors [2–4]. There are already a number of reactions performed successfully in different types of membrane reactors on a laboratory scale [5–18]. In this work a membrane reactor operating in pore flow through mode will be presented. Here the catalyst is immobilized in a porous membrane and is in close contact with the substrate passing the membrane. With a defined pore size, a defined amount of catalyst and a convective mass flow through the porous membrane consecutive reactions should be controlled better than in fixed bed reactors due to a minimized back mixing behavior and improved adjustment of residence time. Fig. 1 demonstrates the process of a heterogeneously catalyzed reaction of the reactants A and B to the desired intermediate product C. The consecutive reaction to the product D should be inhibited. In the fixed bed reactor the selectivity is limited by mass transport due to diffusion processes into and out of the pores of the catalyst. This process increases the residence time of A, B and C at the catalytically active centers which promotes the formation of D. In the membrane diffusion processes can be avoided when the reactants pass the membrane with a convective flow. With the applied flow velocity of 2×10^{-4} m/s convection of the reactant stream is at least one order of

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Abbreviations: c_0, initial concentration; COA, cyclooctane; COD, 1,5-cyclooctadiene; COE, cyclooctene; FBR, fixed bed reactor; FR, flow rate; Ge, Geraniol; h, hour; *k*, reaction rate constant; min, minute; MR, membrane reactor; OIN, 1-octyne; *p*, pressure; PAA, polyacrylic acid; Phac, phenylacetylene; SR, slurry reactor; *T*, temperature; wt.%, weight percent; *X*, conversion

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doi:10.1016/j.cattod.2005.03.073

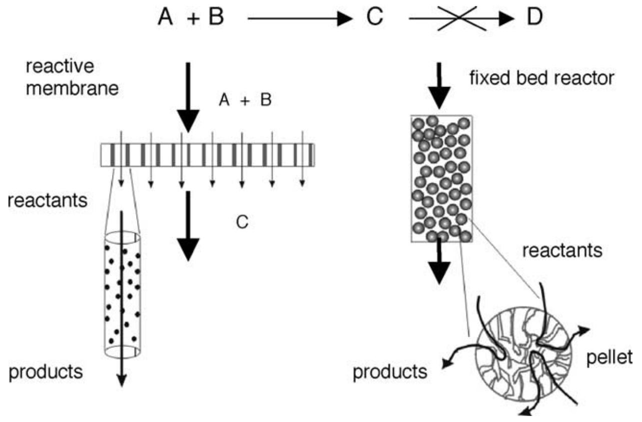


Fig. 1. Catalysis and mass transport in pores, example for a consecutive reaction in a membrane and a catalyst pellet.

magnitude faster than diffusion displacement of molecule in the order of 10^{-5} m within 1 s. As a consequence better selectivities for the intermediate product can be obtained.

In this paper porous membranes made from cross-linked polyacrylic acid (PAA) and activated by immobilized Pd particles are presented. Their catalytic activity and selectivity were investigated in a reactor system constructed as a loop of a saturation vessel and a membrane module for the partial hydrogenations of 1,5-cyclooctadiene to cyclooctene, 1-octyne to octene, phenyl acetylene to styrene and geraniol to citronellol (Figs. 2 and 3).

2. Experimental

2.1. Chemicals

1,5-Cyclooctadiene (99%), 1-octyne (97%), and geraniol (98%) were purchased from Aldrich. Heptane (99%) and phenyl acetylene were received from Fluka. The catalyst Pd/C (0.5 wt.%) was obtained from Degussa-Hüls AG. The catalyst Pd/Al_2O_3 (0.5 wt.%, 3 mm) was obtained from W.C. Heraeus GmbH and from Aldrich. Hydrogen was received from Linde.

2.2. Synthesis of catalytically active polymer membranes

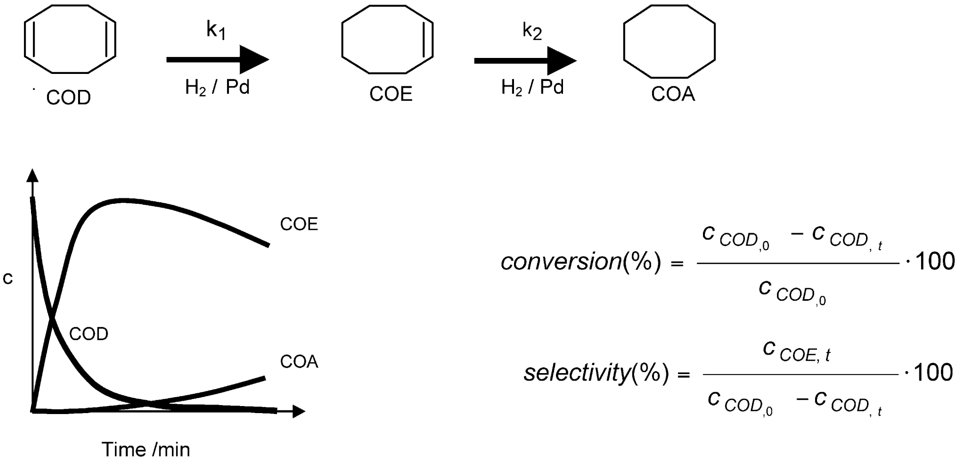
A dispersion of 10 wt.% PAA particles (100 nm diameter) in 1,2,4-trimethylbenzene was produced by precipitation polymerization. The process is described in details in [19]. PAA dispersions of 20 and 30 wt.% were obtained by removing solvent in an ultrafiltration cell. By dissolving palladium(II) acetate in the PAA dispersion with subsequent reduction by $NaBH_4$ Pd nanoparticles with sizes of 3–6 nm were produced. The membranes were prepared by cross-linking the Pd/PAA dispersion with hexanediol-diglycidylether at 80 °C during a time of 48–96 h. After exchange of the solvent 1,2,4-trimethylbenzene against heptane the catalytically active membranes with well-defined pore diameter were obtained (Fig. 4, Table 1).

2.3. Characterization of reactive membranes

The characterization of the palladium nanoparticles in the cross-linked PAA network of the membrane is described in [20]. Table 1 shows the pore radii and the porosity of the produced membranes. No leaching of palladium out of the membranes could be observed in experiments where the membrane was in the solvent stream for several hours.

2.4. Hydrogenation in membrane reactor and fixed bed reactor

The produced membranes were assembled in a membrane reactor (MR) in order to investigate the catalytic activity and selectivity with regard to pore size and for a comparison with standard catalysts. For this comparison the measurements were repeated under the same conditions in a fixed bed reactor (FBR) with commercially available supported catalysts (Pd/Al_2O_3 and Pd/C). Four partial



$$conversion(\%) = \frac{c_{COD,0} - c_{COD,t}}{c_{COD,0}} \cdot 100$$

$$selectivity(\%) = \frac{c_{COE,t}}{c_{COD,0} - c_{COD,t}} \cdot 100$$

Fig. 2. Reaction scheme of hydrogenation of COD, typical concentration profile and definition of conversion and selectivity.

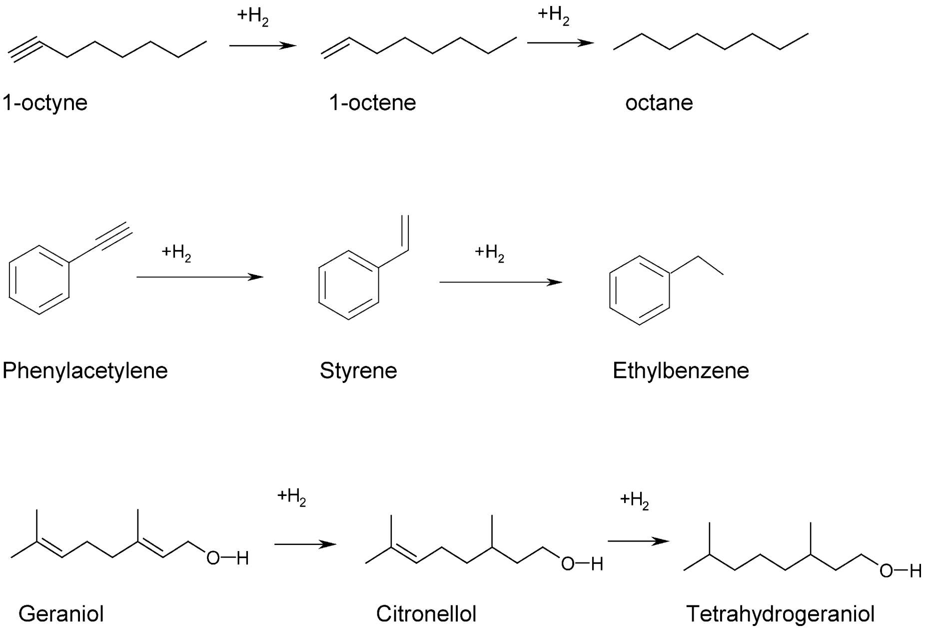


Fig. 3. Reaction scheme of hydrogenation of 1-octyne, phenylacetylene and geraniol.

Fig. 4. Catalytically active membrane (diameter: 65 mm, thickness: 1 mm, Pd-content: 15 mg = 1 wt.%, for pore radii see Table 1).

hydrogenation reactions in liquid phase were chosen: 1,5-cycloctadiene to cyclooctene, 1-octyne to 1-octene, phenylacetylene to styrene and geraniol to citronellol.

Fig. 5a shows a scheme of the reactor system. The hydrogen is fed into a vessel where the reaction mixture is saturated. The saturated solution is passed through the membrane cell and fed back into the saturation vessel. In order to gain complete conversion of the substrates the reaction mixtures were resaturated with hydrogen up to 100 times. The flow rate of the reaction mixture was adjusted between 20 and 40 ml/min. A pressure drop at the membrane was observed to be depending on the flow rate between 0.2 and 1 bar. The reaction took 70–270 min for complete conversion. All experiments were performed at 50 °C and an initial pressure of 40 bar. In all experiments the progress of reaction was monitored by means of decrease of hydrogen pressure from 40 to 25 bar. The concentrations of reactants and products were measured by gas chromatography. For measurements with the catalysts Pd/C and Pd/Al_2O_3 the membrane cell was replaced by a FBR (Fig. 5b). Additionally, the hydrogenation reactions were performed under the same conditions in a slurry reactor (SR) with the catalyst Pd/Al_2O_3 used as a powder (particle diameter 200–300 μm) and as an egg-shell catalyst.

Table 1
Radius of pores and porosity of membranes with different polymer content

Membrane	PAA-concentration (wt.%)	Radius of pores (nm)	Porosity (ε)
I	10	380	70
II	20	230	50
III	30	130	35

3. Results and discussion

3.1. Partial hydrogenation of COD

Fig. 6a compares the time-dependent conversion of the partial hydrogenation of COD in three different reactor systems: MR, FBR and SR. For a comparison of catalysts on different support compromises always have to be found, because not only the support material is changed but also the geometry of the support and the test reactor. Therefore, two systems were chosen here for reference experiments for a benchmarking of the catalytically active membrane. In all experiments 15 mg of palladium were used. Pd-particle size on all supports was about 5 nm. With a Pd/Al_2O_3-powder catalyst with 200–300 μm grain size reaction rate and

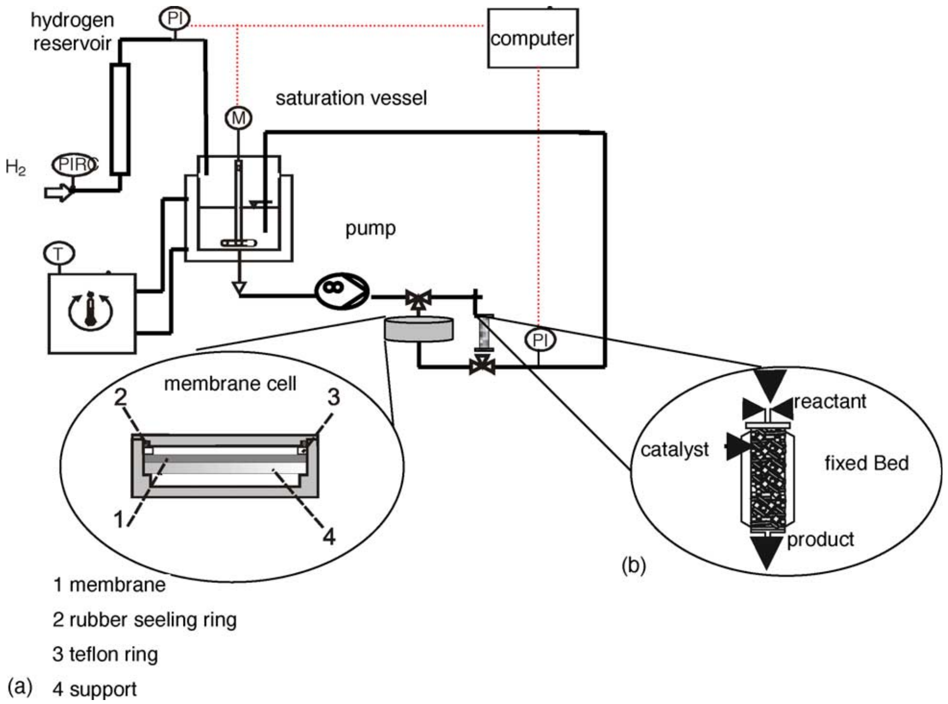


Fig. 5. Schematic diagram of the reactor system for hydrogenation (a) with membrane reactor and (b) with fixed bed reactor.

selectivity unaffected by mass transport phenomena are expected. With a k_la value of $0.15\ s^{-1}$ for the hydrogen transfer the liquid phase may be assumed to be saturated at any time of the reaction. Under these conditions complete conversion is obtained in 20 min with an almost linear increase of conversion with time. The same result is obtained with a well-designed Pd/Al_2O_3 egg-shell catalyst indicating an optimal adjustment of reaction kinetics and mass transport dynamics inside this catalyst. In the MR a complete conversion of COD is achieved after 60 min with using the membrane with the smallest pores. This reactor is operated in a differential mode. During every cycle of the reaction mixture through the membrane the hydrogen concentration decreases strongly. This results in an average hydrogen concentration inside the membrane that is substantially lower than the saturation concentration. As a consequence the reaction rate is lower and more time is needed for complete conversion. With the FBR that is operated in the same differential mode (same residence time per cycle) with catalyst pellets even more time is needed for complete conversion. The influence of different hydrogen concentration profiles in the different reactors is visible in the experiments with the Pd/Al_2O_3 pellets in both reactors. In a differential reactor more time is needed than in a SR with a reaction mixture always saturated with hydrogen. The difference in reaction rates with different supports in the same operating mode in MR and FBR indicates mass transfer limitation of the reaction caused by diffusion inside the pores of the catalyst pellets. The influence of the pore size of the membranes on the reaction rate is shown in Fig. 6b. In the experiment with the membrane with the smallest pores the fastest reaction is observed. This may be explained by a better contact of the reactants with the catalyst inside the smaller pores. With larger pores some reactants could pass the membrane without any contact to the catalyst. In comparison to the catalyst pellets in the FBR a faster conversion of COD is obtained with membrane III (with smallest pores). This shows that mass transport processes that limit the reaction rate are avoided in the MR successfully.

For partial hydrogenation reactions the selectivity for the desired product is even more important than the rate of the reaction. For the discussion of mass transport influences on the reaction kinetics the selectivity data also contain even more information than the conversions. In Fig. 7a the selectivity for cyclooctene is compared for the reaction performed in MR and with catalyst pellets in FBR and SR. The highest selectivity (95% at complete conversion) is obtained in MR and with the egg-shell catalyst in SR. This result indicates that the reaction in the membrane is indeed controlled by the micro kinetics of the reaction, unaffected by mass transport phenomena. With both kind of catalyst pellets applied in FBR substantially lower selectivity (80% for Pd/C and 45% for Pd/Al_2O_3) at complete conversion is observed. This is assumed to be caused by accumulation of cyclooctene inside the catalyst pores due to slow diffusion of cyclooctene out of the pores. In Fig. 7b the selectivity is plotted for membranes with different pore sizes. As already observed for the reaction rate the membrane with smallest pores yields the best results. The selectivity is almost the same as was measured with Pd/Al_2O_3-powder. This again indicates the micro kinetic control of the reaction in this

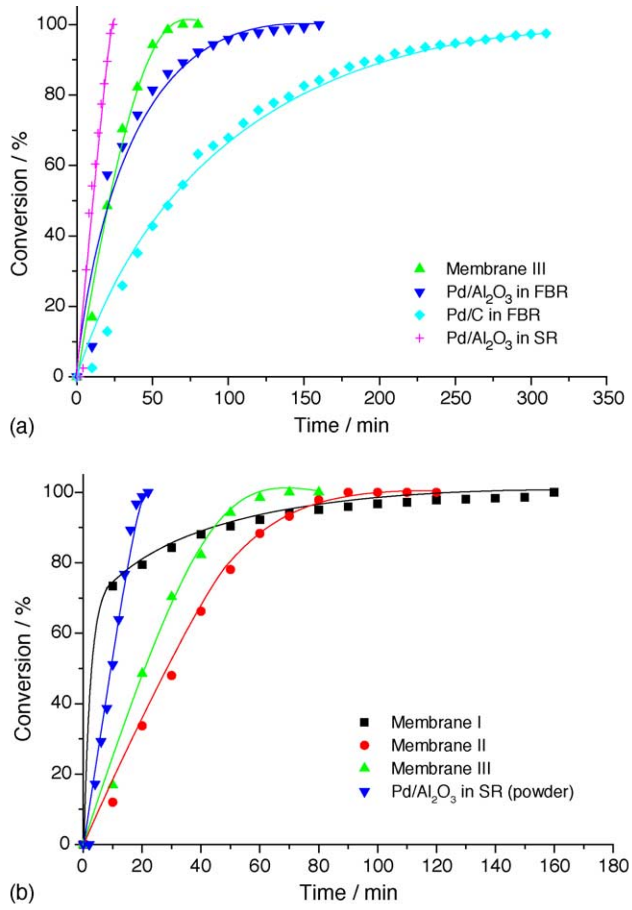


Fig. 6. (a and b) Conversion vs. time for the hydrogenation of COD in MR, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 15 mg, $c_{0,\mathrm{COD}} = 2.33$ mol/l).

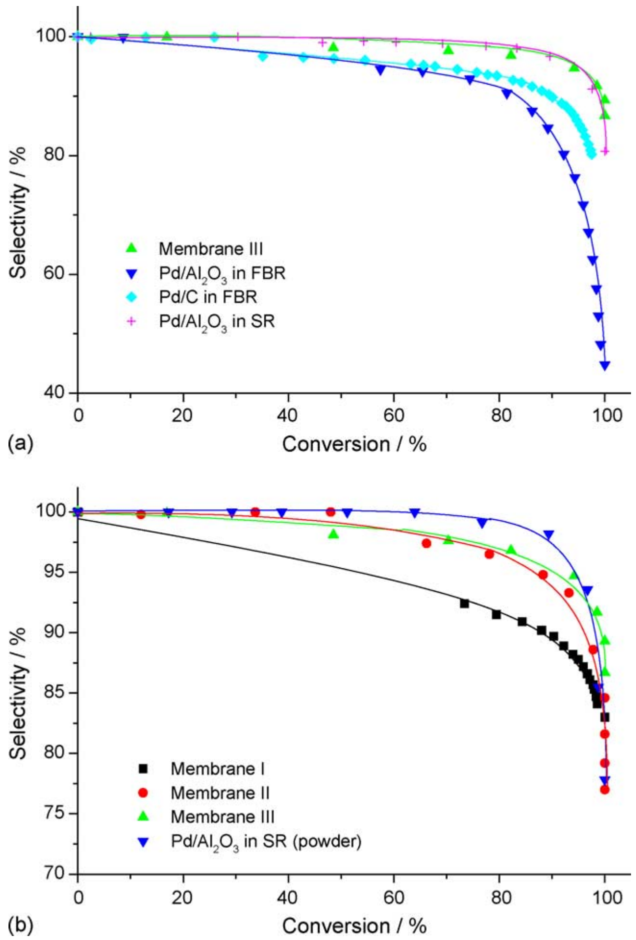


Fig. 7. (a and b) Selectivity vs. conversion for the hydrogenation of COD in MR, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 15 mg, $c_{0,\mathrm{COD}} = 2.33$ mol/l).

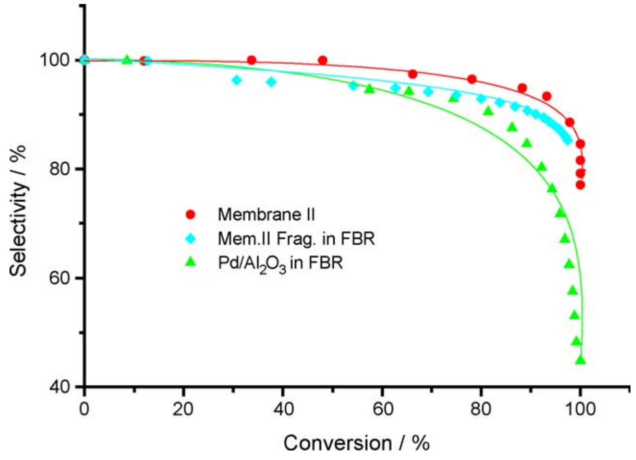


Fig. 8. Selectivity vs. conversion for the hydrogenation of COD in MR and FBR, comparison of membrane II, fragments of membrane II and Pd/Al_2O_3 ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 15 mg, $c_{0,\mathrm{COD}} = 2.33$ mol/l).

membrane. With larger pores less control of selectivity is achieved.

In order to show that the improved selectivity is caused by the avoided disadvantages of mass transport influence on the reaction kinetics rather than by the membrane material, PAA, an experiment with membrane fragments in the FBR is added. In Fig. 8 the results of membrane II and Pd/Al_2O_3 catalyst pellets are compared to the results of fragments of membrane II in the FBR. The fragments produce a slightly lower selectivity than the whole membrane but even higher selectivity than the Pd/Al_2O_3 catalyst. The membrane fragments act as catalyst pellets with palladium particles inside. The reactants have access to the Pd only by diffusion through the pore of the pellets. This results in mass transport influence on selectivity directly. This experiment shows that selectivity is more affected by mass transport than support material.

3.2. Partial hydrogenation of 1-octyne

For partial hydrogenation of 1-octyne the results follow a similar pattern. Again the fastest reaction is observed with Pd/Al_2O_3-powder and egg-shell catalyst in SR (20 min for

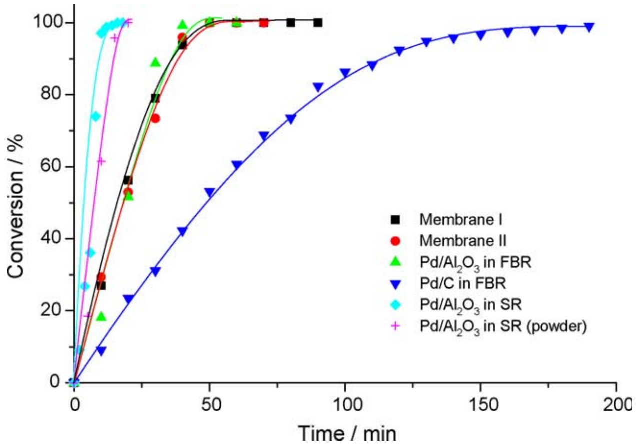


Fig. 9. Conversion vs. time for the hydrogenation of 1-octyne in MR, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 5 mg, $c_{0,\mathrm{OIN}}$ = 1.24 mol/l).

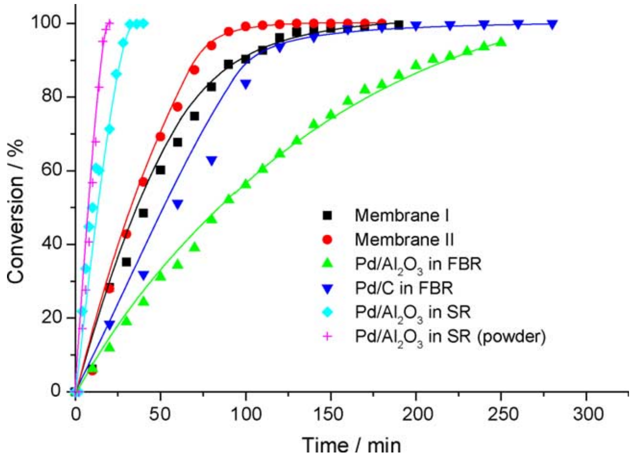


Fig. 11. Conversion vs. time for the hydrogenation of phenylacetylene in MR, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 5 mg, $c_{0,\mathrm{Phac}}$ = 1.66 mol/l).

complete conversion). Pd/PAA-membrane in the membrane module and Pd/Al_2O_3 egg-shell catalyst in FBR need 45 min for complete conversion (Fig. 9). With Pd/C in FBR the reaction rate is strongly retarded by pore diffusion. Selectivity of this reaction appears less sensitive to reaction conditions (Fig. 10). The benchmark of the Pd/Al_2O_3-powder is only met by the catalytically active membrane. The catalyst pellets reach a 5–30% lower selectivity, especially near complete conversion.

3.3. Partial hydrogenation of phenyl acetylene

Fig. 11 shows a comparison of conversions for the hydrogenation of phenyl acetylene in different reactors. The reaction in the MR needs about 120 min for complete conversion. This is faster than in the FBR with catalyst pellets where the reaction is finished after 275 min. The fastest reaction is again obtained in the SR. The slower reaction with the catalyst pellets show that kinetics and mass transport inside the pellets is not well adjusted to phenyl acetylene. With this reaction the egg-shell catalyst performs even worse in reaction rate and selectivity than the Pd/C catalyst. As illustrated in Fig. 12, better selectivity is obtained again with the MR (95% at complete conversion) than in the FBR with catalyst pellets (80%). The same selectivity with Pd/Al_2O_3-powder and Pd/PAA membrane shows micro kinetic control of selectivity. An influence of the membrane pore size is not observed for this reaction. Since both reaction steps (hydrogenation of triple bond and of double bond, respectively) are slower for this reaction than for hydrogenation of COD and 1-octyne there is less chance for mass transport to interfere with the reaction rate.

3.4. Partial hydrogenation of geraniol

The hydrogenation of geraniol is a more demanding reaction for reaction engineering. The two double bonds

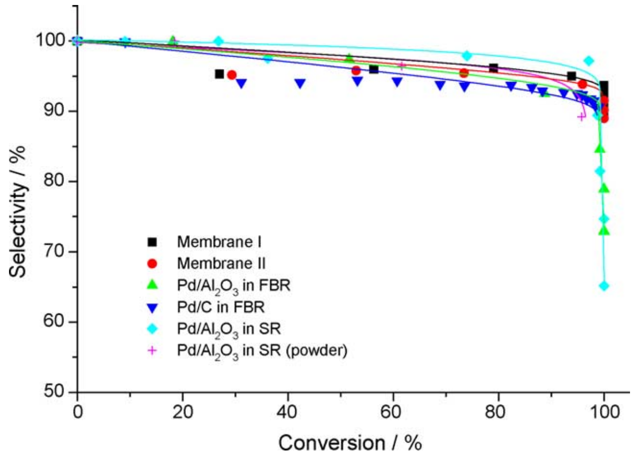


Fig. 10. Selectivity vs. conversion for the hydrogenation of 1-octyne in MR, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 5 mg, $c_{0,\mathrm{OIN}}$ = 1.24 mol/l).

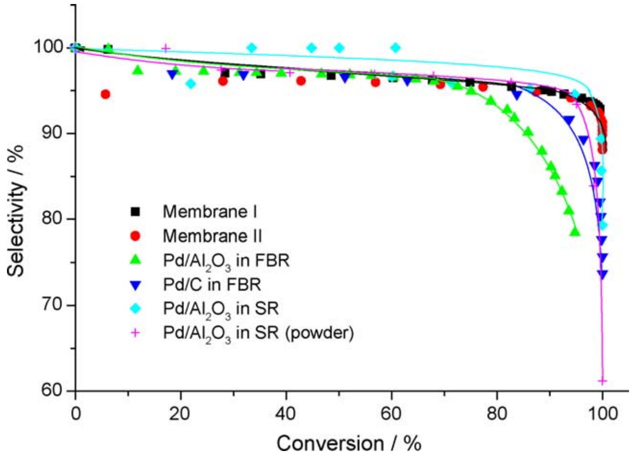


Fig. 12. Selectivity vs. conversion for the hydrogenation of phenylacetylene MR, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 5 mg).

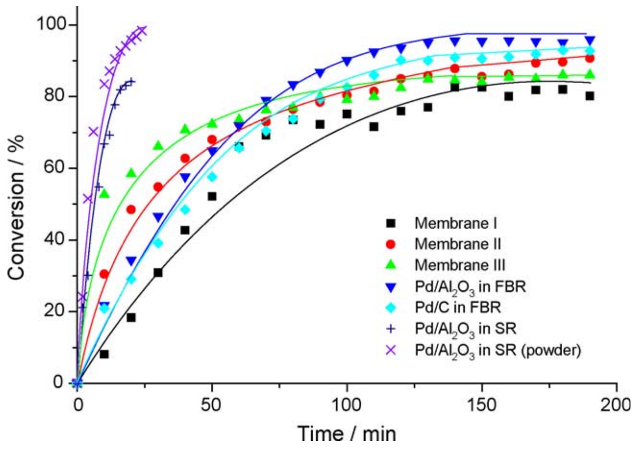


Fig. 13. Conversion vs. time for the hydrogenation of geraniol in Mr, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 15 mg, $c_{0,\mathrm{Ge}} = 0.26$ mol/l).

within the molecule react at about the same rate. Accumulation of the desired product citronellol inside a catalyst support will accelerate the consecutive reaction and decrease the selectivity substantially. Fig. 13 shows the conversions of the hydrogenation of geraniol. In comparison to SR (25 min for complete conversion) the reaction proceeds much slower in the MR and FBR with catalyst pellets (>200 min). There is no pronounced difference in the conversions observed in the two types of reactors operating in differential mode at the same residence time per cycle. But the selectivity for citronellol depends strongly on the applied catalyst. For experimental reasons the selectivity observed at 90% conversion of geraniol is compared for the different catalysts used in MR, FBR and SR (Fig. 14). Again the Pd/Al_2O_3-powder measured in SR serves as benchmark. With all three Pd/PAA membranes up to 15% higher selectivity is obtained in the MR than with this reference catalyst and with the Pd/Al_2O_3 egg-shell catalyst in SR. With both supported catalysts studied under the same conditions in FBR far lower selectivity is determined. With this reaction the unfavorable effects of mass transport limitations on selectivity appear clearly. Among the membrane again the one with narrow pores shows the best performance with 70% selectivity at 90% conversion. The experiment demonstrates that for consecutive reactions with similar rates the pore size needs to be adjusted to the reaction in order to obtain maximum selectivity.

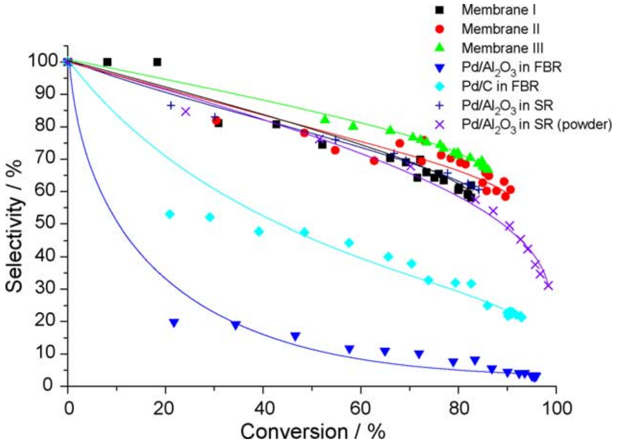


Fig. 14. Selectivity vs. conversion for the hydrogenation of geraniol in Mr, FBR and SR ($T = 50$ °C, $p = 40$ bar, FR = 34 ml/min, Pd amount = 15 mg, $c_{0,\mathrm{Ge}} = 0.26$ mol/l).

3.5. Comparison of substrates

In Table 2 the results of the partial hydrogenation for the chosen reactions are compared from a kinetic point of view. It can be seen that the influence of mass transfer and the selectivity depend on the ratio of the rate constants k_1 and k_2 for the particular reaction steps in consecutive reactions. This ratio was estimated from the series of experiments with Pd/Al_2O_3-powder catalyst. The rate constant k_1 for the hydrogenation of 1-octyne to octene is much higher than for the hydrogenation from 1-octene to octane. Therefore, little influence of mass transfer is observed for the reaction and the selectivity in MR, FBR and SR does not differ very much. For the hydrogenation of phenyl acetylene and COD the rate constant k_1 is also greater than k_2, but the ratio is smaller. In this case, the influence of mass transfer is more significant. This influence can be decreased in MR and SR much better than in the FBR as the selectivity shows. For the hydrogenation of geraniol the influence of mass transfer is strongest, because the rate constants are nearly equal. For this kind of reaction the MR can be a successful alternative to FBR and SR with catalyst pellets. In Table 2 the highest selectivity determined for each reaction in the studied three reactors are assembled. There is an advantage of several percent in selectivity for each reaction performed in the MR compared to FBR or SR. The selectivity obtained in MR is equal to the selectivity obtained with a reference powder catalyst where no mass transport influence on reaction kinetics is expected. This comparison proves that mass transfer limitation on reaction kinetics is avoidable in a membrane reactor operated in pore through flow mode.

Table 2
Comparison of reactions with regard to rate constant, influence of mass transfer and selectivity

Substrate	k_1/k_2	Influence of mass transfer	Selectivity at $X = 100\%$		
			MR	Catalyst pellets	
			Pd/PAA	FBR	SR
Phenylacetylene	$k_1 > k_2$	+	90	70	87
1-Octyne	$k_1 \gg k_2$	−	93	90	95
COD	$k_1 > k_2$	++	90	80	90
Geraniol	$k_1 = k_2$	+++	50	20	40

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