Dehydroalkylation of toluene with ethane in a packed-bed membrane reactor with a bifunctional catalyst and a hydrogen-selective membrane

Seyed Alireza Sadat Rezai and Yvonne Traa*

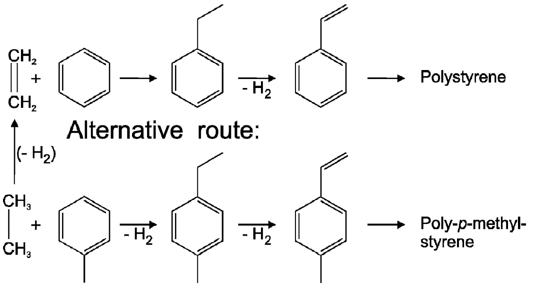
Received (in Cambridge, UK) 14th January 2008, Accepted 19th February 2008
First published as an Advance Article on the web 18th March 2008
DOI: 10.1039/b800486b

The dehydroalkylation of toluene with ethane to form isomeric ethyltoluenes has been carried out in a packed-bed membrane reactor under mild conditions of 350 °C, where it is shown that ethyltoluene yields significantly increase with increasing sweep gas flow rate and pressure.

The alkylation of benzene with ethylene to produce ethylbenzene and, *via* dehydrogenation to styrene and polymerization, finally polystyrene is a commercially important reaction.[1] This "conventional" route (*cf.* Scheme 1) is the largest consumer of valuable benzene. We propose here an "alternative" route, namely the dehydroalkylation of toluene with ethane to ethyltoluenes and, *via* dehydrogenation and polymerization, the production of poly-*p*-methylstyrene. The advantages of the alternative route are manifold: whereas the conventional route starts with expensive ethylene and benzene, in the alternative route the cheaper reactants ethane and toluene are used. This means that intermediate steps, *i.e.*, conversion of ethane to ethylene *via* steamcracking as well as conversion of toluene to benzene *via* toluene disproportionation or toluene hydrodealkylation, can be avoided. In addition, a second molecule of valuable hydrogen can be gained in an easy and cheap manner during the dehydroalkylation of toluene with ethane in a membrane reactor. In theory, additional hydrogen can also be produced in the conventional route if ethylene is produced from ethane steamcracking. However, it is difficult and expensive to recover this hydrogen from the product mixture in steamcrackers. The large disadvantage of the alternative route, though, is the strong thermodynamic limitation: whereas the standard Gibbs energy of reaction for the alkylation of benzene with ethylene at 327 °C amounts to -29 kJ mol^{-1}, the same value for the alternative route, *i.e.*, the reaction of toluene with ethane to *p*-ethyltoluene and hydrogen, is $+41$ kJ mol^{-1}. Thus, the big challenge of the alternative route is to overcome the thermodynamic limitation so that hydrogen can be recovered as a valuable side product.

Hydrogen-selective, Pd-based membranes have been of great interest for a host of reactions,[2–5] in particular for dehydrogenation of alkanes or aromatics where thermodynamic equilibrium is also severely limiting.[6–10] However, the success in the application of membrane reactors to dehydrogenation reactions has been limited. One issue is increased catalyst deactivation in membrane reactors. Since dehydrogenation reactions are highly endothermic, it has not been possible to operate at mild conditions, and at high temperatures removal of hydrogen favors coke formation. Secondly, dehydrogenation reactions result in an increase in the number of moles, so that high pressures impair thermodynamics. This works against membrane reactors, as hydrogen permeation improves with increasing pressure. In the present study, we present the application of hydrogen-selective membranes for a new dehydrogenative-type reaction: namely, the dehydroalkylation of toluene with ethane. Since the net number of moles does not change during this reaction it is possible to operate at higher reaction pressures without sacrificing conversion. Furthermore, due to the thermodynamics of the reaction, it is possible to operate under milder conditions than during the dehydrogenation of alkanes.

Zeolite ZSM-5 was synthesized hydrothermally.[11] After calcination, NH_4^+ and Pd^{2+} ion exchanges were carried out. From elemental analysis, the molar $n_{\mathrm{Si}}/n_{\mathrm{Al}}$ ratio and the amount of Pd were determined to be 40 and 1.0 wt% (referenced to the mass of the dry catalyst), respectively. The catalyst was activated,[11] and thereafter pre-coked using methanol.[12] Catalytic experiments were performed in a tubular packed-bed membrane reactor with a hydrogen-selective membrane (REB Research & Consulting, Ferndale, MI, USA). N_2 was used as an internal standard ($\dot{n}_{\mathrm{ethane}}/\dot{n}_{\mathrm{nitrogen}} \approx 1.5$). The mass of dry catalyst, the reaction temperature, the $\dot{n}_{\mathrm{ethane}}/\dot{n}_{\mathrm{toluene}}$ ratio, and the WHSV (weight hourly space velocity, toluene and ethane) amounted to 0.5 g, (350 ± 4) °C, 7 ± 1, and 2.5 ± 0.2 h^{-1}, respectively. The $\dot{n}_{\mathrm{sweep\ gas}}/\dot{n}_{\mathrm{ethane}}$ ratio was varied between 0.1 and 30 at pressures of 2 and 11 bar on the reaction side and 1 bar on the permeate side. Product analysis was achieved using on-line sampling, with capillary gas chromatography with FID and TCD detectors. From the mass and molar flows, reactant conversion and



Scheme 1 Production of polystyrene polymers.

Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany. E-mail: yvonne.traa@itc.uni-stuttgart.de; Fax: +49 711 685 64065; Tel: +49 711 685 64061

reaction side product selectivities were calculated in wt%. Reaction side yields are based on the toluene conversion.

Fig. 1 shows toluene conversion and product selectivity as a function of time on stream at 2 bar and 350 °C. Toluene conversion is stable throughout the entire experiment at approximately 5%. The same trend applies to product selectivity. Ethyltoluenes selectivity is about 73 wt% during the entire run. The hydrogen selectivity is very low, mainly because of its low molecular mass (selectivities are given in wt%), but also due to transport of hydrogen to the permeate side as well as formation of methane *via* hydrodealkylation of toluene, which consumes hydrogen.[13]

Toluene disproportionation, responsible for the formation of benzene and xylenes, is also limited with about 11 wt% selectivity for each product. Other side products formed in minor amounts include ethylbenzene, propane, and trimethylbenzenes. The improved catalyst stability as compared to other dehydrogenation reactions carried out in membrane reactors may be explained by a combination of pre-coking of the catalyst as well as the milder reaction temperature which does not encourage the formation of coke.† Further results are now given after 90 min on stream, and several experiments have been carried out with the same catalyst, with repetition to ensure reproducibility and on stream stability.

Fig. 2 shows toluene and ethane conversions as a function of $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$. At low $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratios, conversions are low; 4.6 and 0.6% for toluene and ethane, respectively. With increasing $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratios, both toluene and ethane conversions increase, sharply at first, almost doubling at a ratio of 30 to 8.0 and 1.1%, respectively. The increase in conversion is due to improved permeation of hydrogen as it can be removed more efficiently with increasing sweep gas flow rates. This is apparent from Fig. 3, representing the product selectivity as a function of the $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratio. The hydrogen selectivity on the reaction side decreases from 0.7 to 0.4 wt%. This in turn shifts the reaction to form more ethyltoluenes, hence, ethyltoluenes selectivity increases from about 71 to 78 wt% at high sweep gas flow rates. Selectivity for the side products is generally low. Disproportionation of toluene is almost unaffected, whereas methane selectivity decreases from 1.2 to 0.3 wt%; this may be explained by competition of the hydrogen permeation process with the toluene hydrodealkylation reaction for hydrogen. Thus, the membrane helps to avoid this secondary reaction by removing hydrogen.

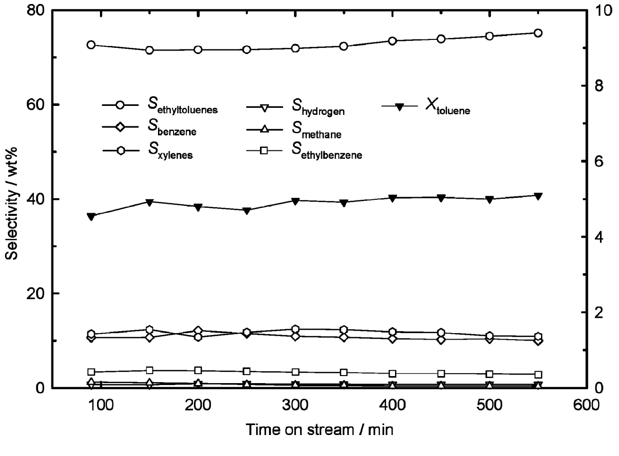


Fig. 1 Time-on-stream behavior for toluene conversion (*X*) and reaction side product selectivity (*S*) in the membrane reactor at 2 bar and 350 °C with $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}} = 0.1$.

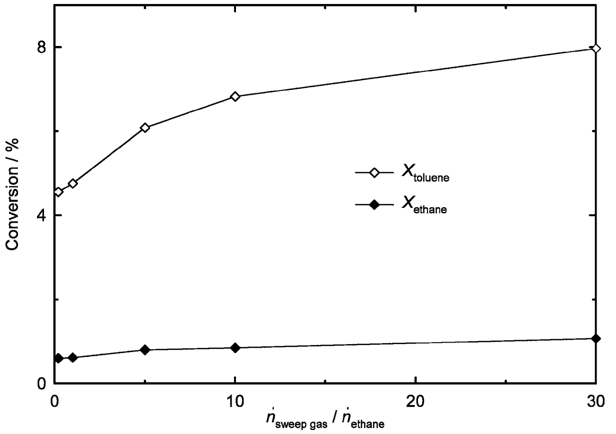


Fig. 2 Toluene and ethane conversion (*X*) as a function of $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ at 2 bar and 350 °C after 90 min on stream.

Table 1 shows the toluene conversion and the yields of important products at varying $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratios at 2 bar and 11 bar. At 2 bar, the yield of the desired ethyltoluenes increases from 3.25 at an $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratio of 0.1 to 6.23 wt% at a ratio of 30, whereas the yields of other products do not increase to such an extent. At a pressure of 11 bar and an $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratio of 10, the conversion has more than doubled to 15.2% as compared to a pressure of 2 bar at the same sweep gas flow rate. However the corresponding ethyltoluenes yield increase is not as significant, reaching only 6.47 wt%. This is due to strongly increased activity for the toluene disproportionation reaction with increasing pressure (combined benzene and xylenes yields of 8.31 wt%),[13,14] therefore suppressing the dehydroalkylation reaction.

Thus, the dehydroalkylation of toluene with ethane can be successfully performed in a membrane reactor. Since the reaction is taking place under mild conditions, the catalytic performance of the bifunctional zeolite in the membrane

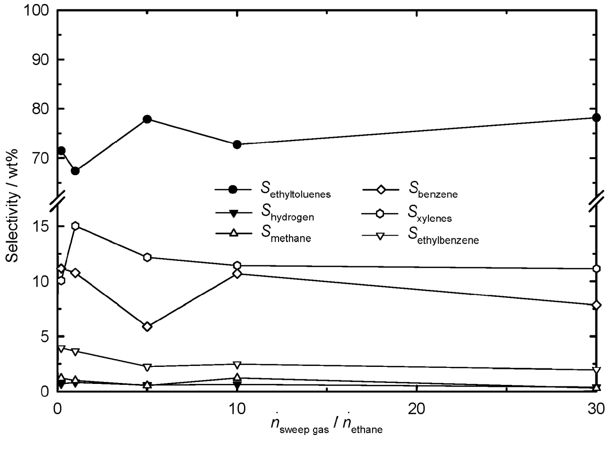


Fig. 3 Reaction side product selectivity (*S*) as a function of $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ at 2 bar and 350 °C after 90 min on stream.

Table 1 Toluene conversion (X) and reaction side yields (Y) at various $\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ ratios and reaction side pressures (P) after 90 min on stream

$\dot{n}_{\text{sweep gas}}/\dot{n}_{\text{ethane}}$ P/bar	0.1 2	10 2	30 2	10 11
X_{toluene}/%	4.55	6.82	7.97	15.2
$Y_{\text{ethyltoluenes}}$/wt%	3.25	4.96	6.23	6.47
Y_{hydrogen}/wt%	0.03	0.04	0.03	0.03
Y_{methane}/wt%	0.05	0.08	0.02	0.09
Y_{benzene}/wt%	0.46	0.73	0.62	4.11
Y_{xylenes}/wt%	0.51	0.78	0.89	4.20

reactor is stable with time on stream. First experiments demonstrate large improvements with tripled conversion and doubled yield to the desired ethyltoluenes by increasing the sweep gas flow rate and the pressure on the reaction side. Increasing pressure has a positive effect on conversion since the net number of moles does not change during this reaction. However, at high pressure, the toluene disproportionation reaction is dominant. Unfortunately, choosing a low contact time to successfully eliminate the toluene disproportionation[15] is not possible here, since under such conditions the produced hydrogen is swept out of the reaction zone before it can permeate.

In conclusion, with regard to yields, the alternative route is clearly inferior to the thermodynamically favored conventional route (*cf.* introduction), where yields larger than 99.5% can be achieved.[1] However, the alternative route is not meant to replace the conventional route. It has the possibility of converting ethane from natural gas into valuable liquid, easy-to-transport chemicals and would be an attractive alternative to flaring natural gas in remote locations where the infrastructure for gas transport is not available. Thus, the unnecessary greenhouse gas emissions and the waste of energy associated with flaring of large amounts of natural gas[16] could be reduced. Hence, the low yields currently achieved in the alternative route should also be seen with regard to the environmental aspect and the trading of carbon dioxide emissions. In addition, taking into account that about 70% of the total production costs of commodity chemicals are due to the raw materials costs,[17] alkane-based processes could, despite lower yields, become economically advantageous. The highest yields achieved in propane dehydrogenation, an industrial process realized for a reaction with similar thermodynamic limitations, are about 50%, but at much higher reaction temperatures around 600 °C,[18] where the thermodynamics are considerably improved. However, the high temperature also causes severe deactivation, and hence, expensive cyclic or continuous catalyst regeneration is necessary.[18]

Finally, it should also be pointed out that the results presented here are only a starting point towards an industrial realization of the alternative route in a membrane reactor. A lot of work still needs to be done. The catalyst used in this study has been pre-coked in order to achieve a stable performance, and pre-coking also reduces the catalyst activity. Therefore, a careful optimization of the catalyst and the reaction conditions in the membrane reactor is needed in order to further achieve industrially relevant yields. In addition, the main isomer produced is *m*-ethyltoluene. This would make costly separation of the isomers necessary in order to obtain pure *p*-ethyltoluene which is favored for polymer production.[19] However, it has been demonstrated during the alkylation of toluene with ethylene that, by modifying the zeolite catalyst, it is relatively easy to achieve isomer distributions with 97% *p*-ethyltoluene.[19] Hence, a similar catalyst modification should also be possible during the dehydroalkylation of toluene with ethane.

Nicole Weiß is acknowledged for help with catalyst synthesis. Financial support by Deutscher Akademischer Austauschdienst is greatly appreciated.

Notes and references

† At a reaction temperature of 400 °C, we observe severe deactivation, with a loss of 65% conversion after 500 minutes on stream compared to the initial activity.

1 T. F. Degnan, Jr, C. M. Smith and C. R. Venkat, *Appl. Catal., A*, 2001, **221**, 283.
2 M. C. Iliuta, F. Larachi, B. P. A. Grandjean, I. Iliuta and A. Sayari, *Ind. Eng. Chem. Res.*, 2002, **41**, 2371.
3 N. Itoh, W. C. Xu, S. Hara, K. Kakehida, Y. Kaneko and A. Igarashi, *Ind. Eng. Chem. Res.*, 2003, **42**, 6576.
4 F. Gallucci, L. Paturzo and A. Basile, *Ind. Eng. Chem. Res.*, 2004, **43**, 2420.
5 K. Sato, T.-a. Hanaoka, S.-i. Niwa, C. Stefan, T. Namba and F. Mizukami, *Catal. Today*, 2005, **104**, 260.
6 E. Gobina, K. Hou and R. Hughes, *Chem. Eng. Sci.*, 1995, **50**, 2311.
7 Y. Yildirim, E. Gobina and R. Hughes, *J. Membr. Sci.*, 1997, **135**, 107.
8 W. Liang and R. Hughes, *Catal. Today*, 2005, **104**, 238.
9 N. Itoh, *AIChE J.*, 1987, **33**, 1576.
10 Y. She, J. Han and Y. H. Ma, *Catal. Today*, 2001, **67**, 43.
11 A. Bressel, T. Donauer, S. Sealy and Y. Traa, *Microporous Mesoporous Mater.*, 2008, **109**, 278.
12 F. Bauer, W.-H. Chen, H. Ernst, S.-J. Huang, A. Freyer and S.-B. Liu, *Microporous Mesoporous Mater.*, 2004, **72**, 81.
13 D. Singer, S. A. Sadat Rezai, S. Sealy and Y. Traa, *Ind. Eng. Chem. Res.*, 2007, **46**, 395.
14 N. R. Meshram, S. G. Hegde, S. B. Kulkarni and P. Ratnasamy, *Appl. Catal.*, 1983, **8**, 359.
15 S. A. Sadat Rezai and Y. Traa, *Catal. Lett.*, 2008, **122**, 91.
16 C. D. Elvidge, E. H. Erwin, K. E. Baugh, B. T. Tuttle, A. T. Howard, D. W. Pack and C. Milesi, *Oil Gas J.*, 2007, **105**(42), 50.
17 J. A. Labinger and G. J. Hutchings, in *Catalytic Activation and Functionalisation of Light Alkanes*, ed. E. G. Derouane, J. Haber, F. Lemos, F. R. Ribeiro and M. Guisnet, Kluwer, Dordrecht, 1998, pp. 455–465.
18 F. Buonomo, S. Sanfilippo and F. Trifiró, in *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, VCH, Weinheim, 1997, vol. 5, pp. 2140–2151.
19 W. W. Kaeding, L. B. Young and A. G. Prapas, *CHEMTECH*, 1982, **12**, 556.