ChemComm

Direct conversion of aromatics into a synthetic steamcracker feed using bifunctional zeolite catalysts

Jens Weitkamp,*[a] Andreas Raichle,[a] Yvonne Traa,[a] Martin Rupp[b] and Franz Fuder[b]

[a] *Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany.*
E-mail: jens.weitkamp@po.uni-stuttgart.de
[b] *VEBA OEL AG, D-45876 Gelsenkirchen, Germany*

Received (in Cambridge, UK) 28th April 2000, Accepted 19th May 2000

Aromatics with 6 to 9 carbon atoms can be converted catalytically with hydrogen on bifunctional zeolites, such as Pd/H-ZSM-5, into a high-quality steamcracker feed, thereby opening a direct route for the utilisation of surplus pyrolysis gasoline.

In view of the predicted over-supply of aromatics,[1] novel catalytic routes for their conversion into valuable products are urgently needed. One of the major sources of aromatics is so-called pyrolysis gasoline, a by-product of steamcracking in which ethylene and propylene are made from light hydrocarbons, such as straight-run naphtha,[2] LPG[3] or ethane. In a preceding communication[4] we have shown that cycloalkanes (which are readily obtained from aromatics by catalytic ring hydrogenation) can be converted on acidic zeolite catalysts, such as H-ZSM-5, into a high-quality steamcracker feed consisting mainly of ethane, propane and *n*-butane. Here, we demonstrate that, as an alternative to this two-stage route (ring hydrogenation followed by ring opening), aromatics can be *directly* converted with hydrogen into the same type of synthetic steamcracker feed, if *bifunctional* zeolite catalysts, *e.g.*, Pd/H-ZSM-5, are used. The literature on catalytic ring opening of aromatics in an excess of hydrogen is very scarce,[5–8] and on the catalysts used so far, the yields of *n*-alkanes with two or more carbon atoms, *i.e.* the most desirable hydrocarbons for a synthetic steamcracker feed, are reported to be low.

Results of the conversion of toluene[9] on 0.2Pd/H-ZSM-5[10] are displayed in Fig. 1. Whereas the conversion of toluene is 100% throughout the temperature range covered, the types of reaction occurring vary drastically: at 200 °C, hydrogenation to methylcyclohexane is the predominant reaction, and part of the methylcyclohexane is isomerised in consecutive reactions *via* the well known[11] bifunctional mechanism into ethylcyclopentane and dimethylcyclopentanes. With increasing temperature, more and more ring opening occurs. At 320 °C, virtually all cyclic hydrocarbons are converted into alkanes,[12] and increasing the temperature further brings about a diminution of the yield of isoalkanes which undergo secondary cracking reactions into propane and ethane. At 400 °C toluene is converted with a yield of 72.8% into C_{2+}-*n*-alkanes (*cf.* Table 1, column 4). It is noteworthy that no aromatics occur in the product under any reaction conditions, and very little methane is formed even at 400 °C. For various reasons (high hydrogen consumption and exothermicity, methane does not form ethylene or propylene in the steamcracker), methane is a very undesired product.

Upon increasing the palladium content of the catalyst from 0.2 to 0.5 and 1.0 wt.%, the yields at a reaction temperature of 400 °C do not change significantly. From this we conclude that, under the conditions applied in this work, ring opening and the formation of light alkanes proceed *via* the bifunctional hydrocracking mechanism[13] and Haag–Dessau cracking,[14] rather than *via* hydrogenolysis[15] on the noble metal.

Table 1 shows results obtained at 400 °C with different feed hydrocarbons. No products other than alkanes were found with any feed hydrocarbon under these conditions. The yields of methane are low throughout (around 3–4%, Table 1, entry 2). Interestingly, the yields of the desired C_{2+}-*n*-alkanes (Table 1, entry 7) do vary significantly with the nature of the aromatic

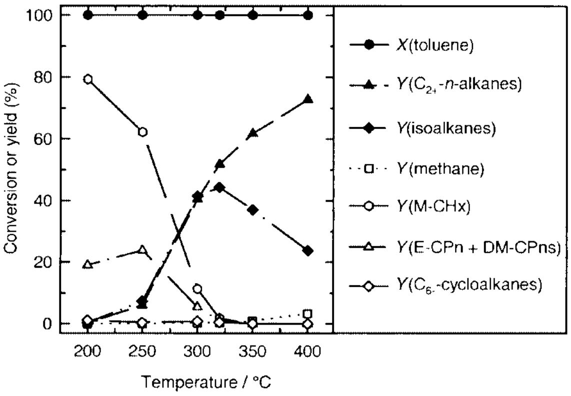

Fig. 1 Conversion of toluene on 0.2Pd/H-ZSM-5 at various temperatures (*X*: conversion; *Y*: yield; M-CHx: methylcyclohexane; E-CPn: ethylcyclopentane; DM-CPns: dimethylcyclopentanes).

Table 1 Conversion of aromatics on 0.2Pd/H-ZSM-5 at 400 °C

		Feed					
Entry		Benzene	Toluene	*o*-Xylene	*p*-Xylene	Ethylbenzene	1,2,4-Trimethylbenzene
1	X^a (%)	100	100	100	100	100	100
2	$Y_{\text{methane}}{}^b$ (%)	3.7	3.3	4.0	4.1	2.5	3.0
3	$Y_{\text{ethane}}{}^b$ (%)	14.4	7.9	15.6	14.9	30.6	13.6
4	$Y_{\text{propane}}{}^b$ (%)	62.8	48.6	49.1	46.7	49.0	49.4
5	$Y_{n\text{-butane}}{}^b$ (%)	11.9	15.9	14.2	15.0	9.5	15.2
6	$Y_{C_{5+}\text{-}n\text{-alkanes}}{}^b$ (%)	1.2	0.4	3.4	3.8	1.1	2.7
7	$Y_{C_{2+}\text{-}n\text{-alkanes}}{}^{b,c}$ (%)	90.3	72.8	82.3	80.4	90.2	80.9
8	$Y_{\text{isoalkanes}}{}^b$ (%)	6.0	23.9	13.7	15.5	7.3	16.1

[a] *X* is the conversion of the aromatic feed hydrocarbon. [b] *Y* is the yield of the product indicated and defined in the usual manner, *e.g.*, $Y_{n\text{-butane}} = (4/7) \times (\dot{n}_{n\text{-butane, out}}/\dot{n}_{\text{toluene, in}})$, $\dot{n}$ being the molar flux. [c] Sum of entries 3 to 6.

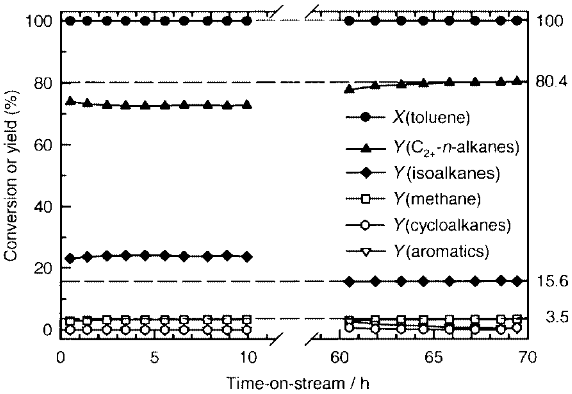

Fig. 2 Coke selectivation in the conversion of toluene on 0.2Pd/H-ZSM-5. (During the initial 10 h and from 60 to 70 h on-stream time, the reaction temperature was 400 °C. In the period between 10 h and 60 h, lower reaction temperatures in the range from 200 to 350 °C were applied; *X*: conversion; *Y*: yield.)

feed hydrocarbon. This yield is lowest for toluene and above 90% for both benzene and ethylbenzene. Note also that very large amounts of propane are formed from benzene (which can be rationalized in terms of a so-called type C β-scission[16,17] of hexyl cations), while an unusually high yield of ethane is observed in the product from ethylbenzene (which we tentatively ascribe to a deethylation reaction).

Regardless of the hydrocarbon used as feed, there was no significant change in the product yields with time-on-stream. In Fig. 2, results are shown which were obtained with toluene as feed on 0.2Pd/H-ZSM-5. During the initial 10 h, the yield of C_{2+}-*n*-alkanes amounted to *ca.* 73%. For the next 50 h (not shown in Fig. 2) toluene was converted on this catalyst sample at lower temperatures in the range 200–350 °C. Thereafter, the reaction temperature was again raised to 400 °C for 10 h. Significantly better yields of the desired C_{2+}-*n*-alkanes (*ca.* 80%) were attained than with the fresh catalyst. We interpret this selectivity gain in terms of a so-called coke selectivation, *i.e.* at the lower reaction temperatures between the two runs at 400 °C, some dimerization and/or disproportionation reactions of methylcyclohexane[18] or toluene inside the zeolite pores must have taken place, whereby larger product molecules were formed which ultimately led to some carbonaceous deposits with a concomitant narrowing of the pores. Similar effects have been observed by others, *e.g.* in the disproportionation of toluene on H-ZSM-5.[19]

In conclusion, we have demonstrated that aromatics can be *directly* converted with hydrogen into a high-quality steamcracker feed on bifunctional zeolite catalysts of the Pd/H-ZSM-5 type. This direct route will have to compete with the two-stage variant consisting of ring hydrogenation in the aromatics over a hydrogenation catalyst followed by ring opening of cycloalkanes on monofunctional zeolites.[4] The main technological advantage of the direct route described here is a single catalytic reactor for the manufacture of synthetic steamcracker feed from pyrolysis gasoline. On the other hand, advantageous features of the two-stage variant are (i) the possibility to optimise the ring hydrogenation of aromatics and the ring opening of the resulting cycloalkanes separately and (ii) the generation of the exothermic heat in two separate reactors and, hence easier removal of this heat. It remains to be seen whether the direct route or the two-stage variant is economically more attractive.

Notes and references

1 W. J. Petzny and C.-P. Hälsig, in *DGMK Tagungsbericht 9903, Proc. DGMK Conference: The Future Role of Aromatics in Refining and Petrochemistry, October 13-15, 1999, Erlangen, Germany*, ed. G. Emig, M. Rupp and J. Weitkamp, DGMK, Hamburg, 1999, p. 7.
2 Straight-run naphtha is a light petroleum fraction composed essentially of C_5 and C_6 hydrocarbons.
3 LPG stands for Liquefied Petroleum Gas, the C_3 and C_4 hydrocarbons from petroleum.
4 J. Weitkamp, A. Raichle, Y. Traa, M. Rupp and F. Fuder, *Chem. Commun.*, 2000, 403.
5 T. Sano, K. Okabe, H. Hagiwara and H. Takaya, *J. Mol. Catal.*, 1987, **40**, 113.
6 J.-K. Chen, A. M. Martin, Y. G. Kim and V. T. John, *Ind. Eng. Chem. Res.*, 1988, **27**, 401.
7 L. P. Poslovina, V. G. Stepanov, L. V. Malysheva, E. A. Paukshtis, L. A. Vostrikova and K. G. Ione, *Stud. Surf. Sci. Catal.*, 1997, **105**, 997.
8 A. Chambellan, O. Cairon and T. Chevreau, in *Proc. 12th Int. Zeolite Conf., Warrendale, USA, July 5–10, 1998*, ed. M. M. J. Treacy, B. K. Marcus, M. E. Bisher and J. B. Higgins, Materials Research Society, Baltimore, 1999, p. 1025.
9 Toluene is a major constituent of pyrolysis gasoline, other typical aromatics in pyrolysis gasoline are ethylbenzene, xylenes and benzene.
10 Zeolite ZSM-5 (n_{Si}/n_{Al} = 20) was hydrothermally synthesised after S. Ernst and J. Weitkamp, *Chem. Ing. Tech.*, 1991, **63**, 748, ion-exchanged with aqueous solutions of NH_4NO_3 and $Pd(NH_3)_4Cl_2$ and pre-treated successively in flows of air (12 h), nitrogen (1 h) and hydrogen (7 h) at 400 °C to yield bifunctional catalysts with $m_{Pd}/m_{dry\ zeolite}$ = 0.2, 0.5 or 1.0% referred to as 0.2Pd/H-ZSM-5, 0.5Pd/H-ZSM-5 and 1.0Pd/H-ZSM-5, respectively. The experiments were performed in a flow-type stainless steel apparatus with a fixed-bed reactor. The mass of dry catalyst (particle size between 0.20 and 0.32 mm), the total pressure (which was virtually equivalent to the partial pressure of hydrogen), the partial pressure of the aromatic feed hydrocarbon at the reactor inlet and the weight hourly space velocity (WHSV) amounted to 500 mg, 6.0 MPa, 65 kPa and 0.68 h^{-1}, respectively. Product analysis was achieved by capillary gas chromatography.
11 J. Weitkamp, P. A. Jacobs and S. Ernst, *Stud. Surf. Sci. Catal.*, 1984, **18**, 279.
12 The product yields at 320 °C are: methane 0.5%, ethane 1.0%, propane 41.3%, *n*-butane 7.4%, *n*-pentane 1.7%, *n*-hexane 0.5%, isobutane 40.7%, isopentane 2.3%, isohexanes 1.3%, isoheptanes 0.1%, cycloalkanes 3.3%.
13 J. Weitkamp, in *Ketjen Catalysts Symposium 1988: Fluid Catcracking, Hydrocracking, Hydrotreating, Pt-Reforming*, ed. H. J. Lovink, Akzo Chemicals, Amersfoort, 1988, p. G-3 1.
14 (*a*) W. O. Haag and R. M. Dessau, in *Proc. 8th Int. Congr. Catal., July 2–6, 1984, Berlin, Germany*, vol. 2, Verlag Chemie, Weinheim, 1984, p. 305; (*b*) S. Kotrel, H. Knözinger and B. C. Gates, *Microporous Mesoporous Mater.*, 2000, **35–36**, 11.
15 F. G. Gault, *Adv. Catal.*, 1981, **30**, 1.
16 β-Scission of alkylcarbenium ions—a scission of the carbon–carbon bond in the β-position with respect to the positively charged carbon atom—is the key step in the bifunctional hydrocracking mechanism.
17 J. Weitkamp, P. A. Jacobs and J. A. Martens, *Appl. Catal.*, 1983, **8**, 123.
18 H. Schulz, J. Weitkamp and H. Eberth, in *Proc. 5th Int. Congr. Catalysis*, ed. J. W. Hightower, North-Holland, Amsterdam, 1973, vol. 2, p. 1229.
19 L.-Y. Fang, S.-B. Liu and I. Wang, *J. Catal.*, 1999, **185**, 33.