Preparation of synthetic steamcracker feed from cycloalkanes (or aromatics) on zeolite catalysts

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Methylcyclohexane is converted into a high-quality steamcracker feed over acidic zeolites with appropriate pore systems, thereby opening a new route for the utilisation of surplus aromatics.

Steamcrackers[1] are widely employed for the production of ethylene and propylene from naphtha,[2] ethane or similar light hydrocarbons. One of the by-products of steamcracking is pyrolysis gasoline which is rich in aromatics. Given the forecasted growth in the worldwide demand of ethylene[3] and propylene[4] from, respectively, 57 × 10^6 and 30 × 10^6 tonne yr^{-1} in 1990 to *ca.* 140 × 10^6 and 75 × 10^6 tonne yr^{-1} in 2010, the production of pyrolysis gasoline will necessarily increase as well. Up till now, pyrolysis gasoline has been used as an aromatics-rich and, hence, high-octane petrol component. With the so-called Auto Oil Programme of the European Community, the aromatics content of petrol has to be diminished from 45 to <42 vol% until the year 2000, and to <35 vol% until 2005.[5] Therefore, new outlets for surplus aromatics are urgently needed. We report here on a novel catalytic chemistry by which cycloalkanes (or aromatics, since these can easily be hydrogenated into cycloalkanes by state-of-the-art processes) are converted predominantly into light linear alkanes (ethane, propane, *n*-butane and *n*-pentane) the mixture of which is a premium steamcracker feedstock for high ethylene and propylene yields.[6]

Previous work on ring opening of cycloalkanes mostly relies on hydrogenolysis over noble metal catalysts designed predominantly to yield branched alkanes.[7–9] Such hydrocarbons are, however, less suitable as a steamcracker feed, since large amounts of undesired methane will be formed. Only few reports deal with cracking of cyclic hydrocarbons over acidic zeolites in an excess of hydrogen,[10–12] and yields of *n*-alkanes during the conversion of cycloalkanes or aromatics with seven or more carbon atoms are reported to be low.

On zeolite H-ZSM-5 at 400 °C, methylcyclohexane is converted[13] with a yield of 70.6% into ethane (9.4%), propane (47.7%), *n*-butane (12.4%) and *n*-pentane (1.1%), see Fig. 1 and Table 1, whereas on zeolite H-Y, much lower yields (42.8%) of these desirable products are obtained. On H-ZSM-5, the most important by-products are branched alkanes, *viz.* 17.6% isobutane, 6.2% isopentane and 0.6% isohexanes. Whereas on H-ZSM-5 virtually no aromatics are found, the total yield of aromatics on H-Y amounts to 15.9% (benzene 2.2%, toluene 6.4%, C_8-aromatics 5.6% and C_9-aromatics 1.7%). We tentatively attribute this difference to the lower activity of the larger-pore zeolite for cleavage of endocyclic carbon–carbon bonds.[14] The difference in selectivities becomes even more pronounced at lower conversions (Fig. 2) or at high times-on-stream (Table 1, entry 7). The deactivation observed on zeolite H-Y correlates qualitatively with the mass ratio of carbon in the coke formed on the catalyst[15] and in the methylcyclohexane fed (Table 1, entry 8).

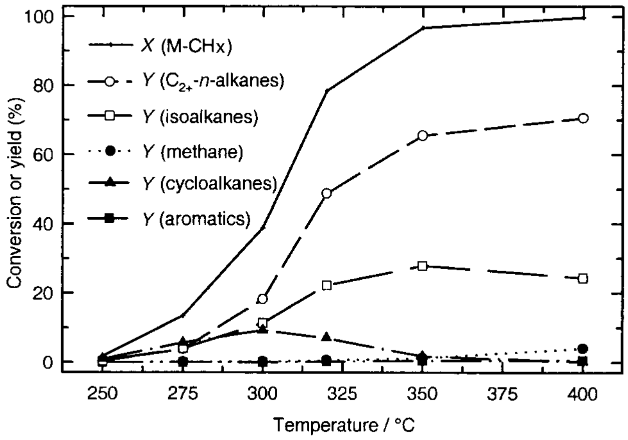

Fig. 1 Conversion of methylcyclohexane on H-ZSM-5 at various temperatures.

The pronounced differences in the catalytic behaviour of both zeolites can be accounted for by introducing the so-called cracking mechanism ratio,[16] CMR ≡ $(Y_{\text{methane}} + Y_{C_2\ \text{hydrocarbons}})/Y_{\text{isobutane}}$ (Table 1, entry 9 and Fig. 3), which is considered as a quantitative measure for the relative contributions of monomolecular Haag–Dessau cracking[17] *versus* conventional bimolecular cracking. In the narrower pores of zeolite ZSM-5 and with increasing temperature, Haag–Dessau cracking, which produces large amounts of ethane and propane, is favoured over the spatially more demanding bimolecular mechanism which leads predominantly to isobutane. In line with this interpretation, much more hydrogen is incorporated into the cracked products on H-ZSM-5 than on H–Y (Table 1, entry 10): Clearly, H_2 can be activated on acidic zeolites, as demonstrated previously.[12,18,19]

In conclusion, methylcyclohexane can be converted over acidic zeolites with suitable pore systems into a high-quality synthetic steamcracker feed consisting predominantly of eth-

Table 1 Conversion of methylcyclohexane at 400 °C and 30 min TOS[a]

Entry	Catalyst	H-ZSM-5	H-Y
1	$X_{\text{M-CH}x}$ (%)	99.9	99.5
2	Y_{methane} (%)	4.0	0.6
3	$Y_{n\text{-alkanes}}$[b] (%)	70.6	42.8
4	$Y_{i\text{-alkanes}}$ (%)	24.4	39.3
5	$Y_{\text{cycloalkanes}}$ (%)	0.2	0.8
6	$Y_{\text{aromatics}}$ (%)	0.7	15.9
7	$Y_{n\text{-alk.}}$[b](440 min TOS)/$Y_{n\text{-alk.}}$ (30 min TOS)	1.00	0.84
8	$m_{\text{C, coke}}/m_{\text{C,M–CH}x}$[c] (%)	<0.05	1.76
9	CMR[d]	0.76	0.15
10	H_2 incorporation[e]	2.3	1.2

[a] Time-on-stream. [b] Yield of *n*-alkanes = $Y_{\text{ethane}} + Y_{\text{propane}} + Y_{n\text{-butane}} + Y_{n\text{-pentane}}$, the individual yields being defined in the usual manner, *e.g.* $Y_{\text{ethane}} = (2/7) \times (\dot{n}_{\text{ethane, out}}/\dot{n}_{\text{M–CH}x\text{, in}})$. [c] Mass ratio of carbon in the coke formed on the catalyst after 500 min time-on-stream and in the methylcyclohexane cumulatively fed within the same time. [d] Cracking mechanism ratio, see text. [e] $\dot{n}_{H_2\text{, consumed}}/\dot{n}_{\text{M–CH}x\text{, fed}}$.

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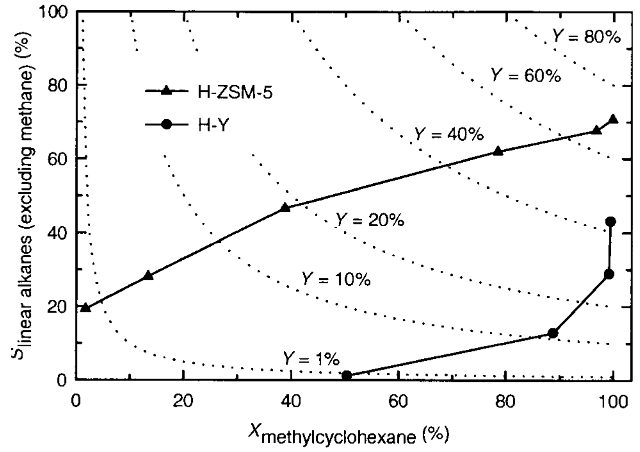

Fig. 2 Selectivity to linear alkanes (excluding methane) as a function of the methylcyclohexane conversion on zeolites H-ZSM-5 and H-Y after 30 min TOS.

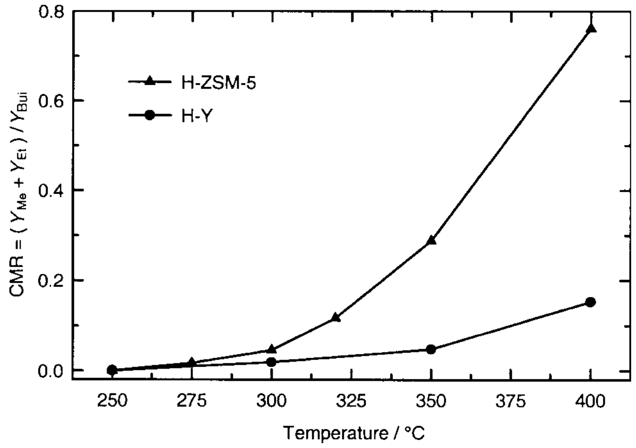

Fig. 3 Cracking mechanism ratio (CMR) after 30 min TOS as a function of temperature during the conversion of methylcyclohexane.

ane, propane and *n*-butane, thereby opening a new route for the utilisation of surplus aromatics. Instead of hydrogenating the aromatics to cycloalkanes and converting the latter into light *n*-alkanes separately, one can use a bifunctional form of the zeolite, such as Pd/H-ZSM-5 or Pt/H-ZSM-5, and produce light *n*-alkanes directly from aromatics in a single reactor. Such work is under way in our laboratories.

Notes and references

1 In steamcrackers, hydrocarbons are thermally cracked in the presence of steam as diluent.

2 Light petrol, especially hydrocarbons with five and six carbon atoms.

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