Experimental Section

In a 250-mL bulb $LiC(SiMe_3)_3$ (1.5 g, 6.3 mmol) was placed in toluene (25 mL). After the solution had been cooled to $-78\,^{\circ}C$, GaBr (15 mL of a 0.3 M solution in toluene/THF (3/1), 5 mmol) was added. The reaction mixture was slowly allowed to warm to room temperature, during which the solution became dark red to black. The solvent was then removed in vacuum. The black residue was extracted with pentane. A few black crystals of **1** in the form of hexagonal platelets precipitated from the dark brown pentane extract.

Crystal structure data of **1**: $Ga_8(C(SiMe_3)_3)_6$, $M_r = 1891.3$, crystal dimensions $0.3 \times 0.6 \times 0.6$ mm, monoclinic *c*, space group $C2/m$, $a = 13.203(3)$, $b = 24.704(5)$, $c = 17.382(4)$ Å, $\beta = 103.86(3)^{\circ}$, $V = 5504.3(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.175\,g\,cm^{-3}$, $\mu_{Mo} = 2.150\,mm^{-1}$, $2\theta_{max} = 51.74^{\circ}$, 16186 measured reflections, 5446 independent reflections ($R_{int} = 0.0841$), absorption correction: numerical (min./max. transmission 0.1630/0.4012), $R_1 = 0.0466$, $wR_2 = 0.1388$. Stoe-IPDS diffractometer ($Mo_{K\alpha}$ radiation, ($\lambda = 0.71073$ Å), 200 K). The structure of **1** was solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXTL (G. M. Sheldrick, Universität Göttingen). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151247. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Haag–Dessau Catalysts for Ring Opening of Cycloalkanes

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With the advent of the Auto Oil Programme of the European Union, the aromatics content of gasoline has to be reduced from 45 vol% in 1999 to 42 and 35 vol% in 2000 and 2005, respectively.[1] Therefore, western Europe will probably face a surplus of aromatics, especially toluene, soon. One of the major sources of aromatics is pyrolysis gasoline, a by-product from steamcracking of naphtha for the production of ethene and propene. Given the large growth rate of demand for ethene[2] and propene[3] that is generally forecasted, the production of pyrolysis gasoline—and, hence, of aromatics—will necessarily increase as well. For the conversion of aromatics into a premium synthetic steamcracker feedstock (consisting mainly of ethane, propane, and *n*-butane), two process variants have recently been introduced. In variant 1, the aromatics are directly converted with hydrogen on a bifunctional zeolite catalyst;[4] in variant 2, cycloalkanes, which can easily be obtained from aromatics by state-of-the-art hydrogenation processes, are hydroconverted on acidic zeolite catalysts.[5] In both cases, pyrolysis gasoline is ultimately recycled into the steamcracker and thus removed from the market.

Recently, we observed that the selectivity to *n*-alkanes with two and more carbon atoms (C_{2+}-*n*-alkanes) is very high during the conversion of methylcyclohexane on catalysts that contain noble metals in such small amounts that they can be classified neither as typically bifunctional nor as monofunctional. We report here on these results and their mechanistic implications.

To begin with, the salient mechanistic features of catalytic ring opening of cycloalkanes are briefly sketched (Scheme 1): On bifunctional catalysts, methylcyclohexane is dehydrogenated on metallic sites, and the resulting cycloalkenes are protonated to carbenium ions on acidic sites. Usually, skeletal isomerization into highly branched isomers occurs first, whereupon classical β-scission can proceed. Finally, the diene formed is hydrogenated on a metal site (Scheme 1a, top).[6, 7] On monofunctional acidic catalysts, two different mechanisms can be operative:[8, 9] On the one hand, β-scission of classical carbenium ions is possible, but the latter can now only form through a bimolecular hydride transfer (Scheme 1a, bottom). On the other hand, methylcyclohexane can be directly protonated forming a nonclassical carbonium ion with a three-center, two-electron bond in the transition state (Haag–Dessau cracking, Scheme 1b). If ring opening is accompanied by secondary cracking steps, isoalkanes (no

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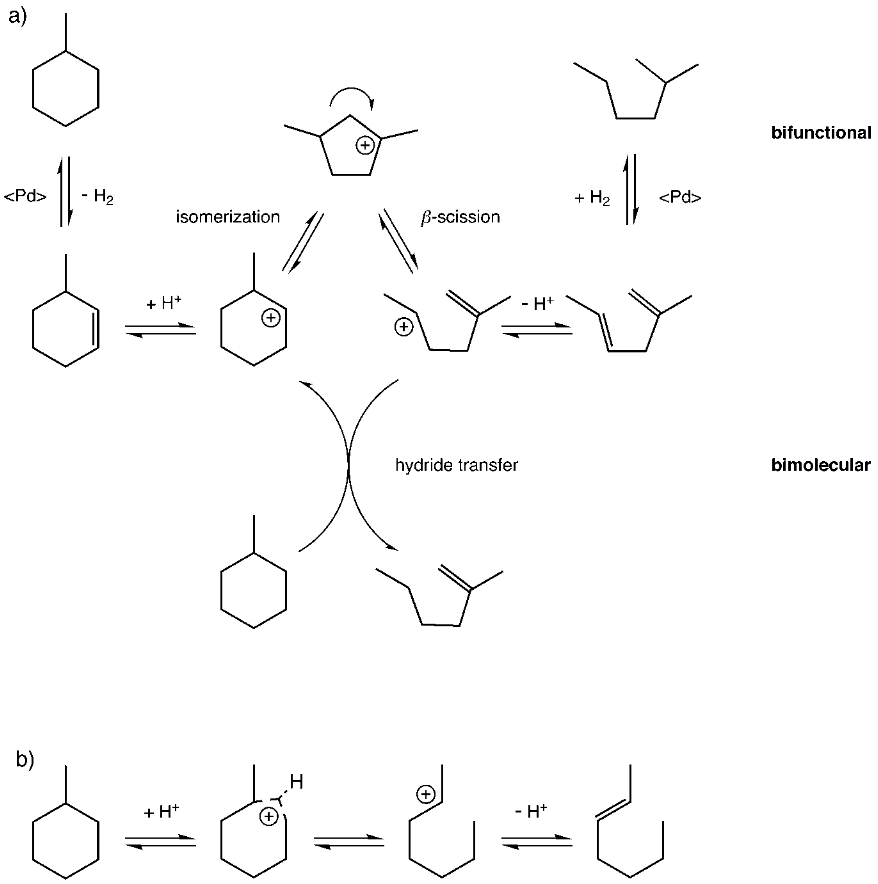

Scheme 1. Mechanisms for ring opening of cycloalkanes: a) classical (bifunctional or bimolecular) and b) nonclassical cracking.

methane and ethane due to the instability of primary carbenium ions) will predominantly be formed in the first case due to the preceding isomerization, while *n*-alkanes (including methane and ethane) will be the dominant products in the second case. Under increased pressure of hydrogen, only saturated compounds and no alkenes are obtained in the product stream, even on the metal-free acidic catalysts. This can be accounted for by activation of hydrogen on the acid sites.[5] As a measure of the contribution of the two mechanisms, Wielers et al.[10] introduced the so-called cracking mechanism ratio (CMR), which is defined as the ratio of the yields of C_1 and C_2 hydrocarbons to the yield of isobutane.

On the basis of these generally accepted mechanistic concepts, an attempt will be made to rationalize the experimental data obtained on H-ZSM-5 zeolites. During the conversion of methylcyclohexane at 250 °C, three types of reactions can be observed on all catalysts: a) isomerization to ethylcyclopentane and dimethylcyclopentanes, b) ring opening to *n*-heptane and its isomers, and c) secondary cracking to propane and isobutane or *n*-butane (Figure 1). The formation of all these products can readily be accounted for by reactions via carbenium ions; no contribution of nonclassical Haag–Dessau cracking has to be invoked at this low reaction temperature. On the typically bifunctional catalysts (0.2 or 1.0 wt% Pd), the conversion is clearly higher (approximately 9%) than on the catalysts with no or only small amounts of palladium (approximately 3%). In addition, the isomerization products are formed with considerably higher selectivity on the bifunctional catalysts, whereas the selectivities to the secondary cracking products remain comparably small, which indicates an efficient desorption mechanism on these catalysts:[6] At this low conversion, methylcyclohexene molecules formed on metal sites displace the products of isomerization or ring opening from the acidic sites to a large extent before secondary cracking can take place.

On all catalysts, the yields of cycloalkanes and of isoalkanes exhibit maxima and then start to decrease with increasing conversion (Figure 2), whereas the yields of C_{2+}-*n*-alkanes (the desired synthetic steamcracker feedstock) and methane (a very undesirable product) increase monotonously. This could be due to ever faster cracking reactions and to an increasing influence of nonclassical Haag–Dessau cracking. A closer examination of the temperature dependence of C_{2+}-*n*-alkane formation reveals significant differences between the various catalysts (Figure 3): On the typically bifunctional catalysts, the selectivities to C_{2+}-*n*-alkanes are considerably smaller than those on the monofunctional acidic catalyst, and this is true for all temperatures applied. In contrast, on the catalysts with 10 or 100 ppm of palladium, slightly less C_{2+}-*n*-alkanes are formed at low temperatures compared to the acidic catalyst, but significantly more at 400 °C. With the temperature dependence of the CMR value depicted in Figure 4, these differences become even more striking: On all catalysts, the CMR value, and hence the proportion of nonclassical cracking via carbonium

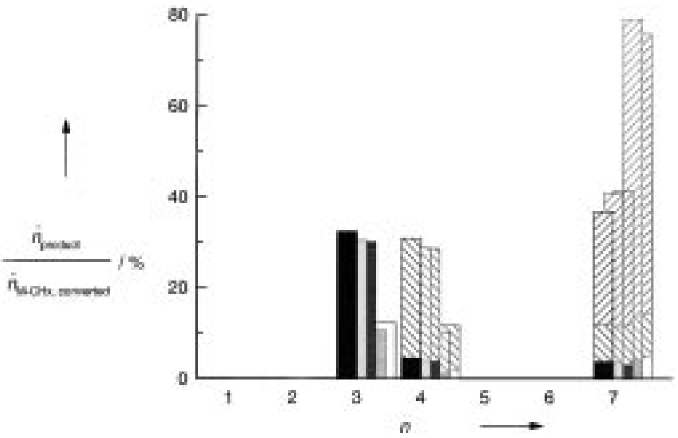

Figure 1. Molar fractions of the products with *n* carbon atoms during the conversion of methylcyclohexane on H-ZSM-5 catalysts with 0 (black), 0.001 (light gray), 0.01 (dark gray), 0.2 (medium gray), and 1.0 (white) wt% of palladium at 250 °C. Forwards shading (///): cycloalkanes; backwards shading (\\\): isoalkanes; solid color: *n*-alkanes; aromatics are not formed.

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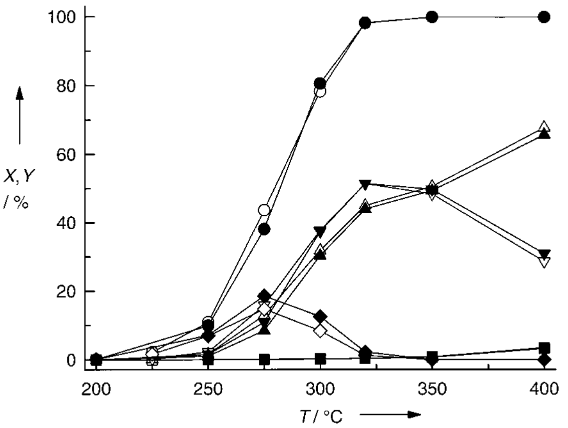

Figure 2. Temperature dependence of the conversion of methylcyclohexane on zeolite H-ZSM-5 with 0.2 wt% of palladium (full symbols) or 0.4 wt% of platinum (open symbols). X: conversion, Y: yield. ○, ●: X(methylcyclohexane); △, ▲: Y(C_{2+}-n-alkanes); ▽, ▼: Y(isoalkanes); □, ■: Y(methane); ◇, ◆: Y(cycloalkanes); aromatics were not formed.

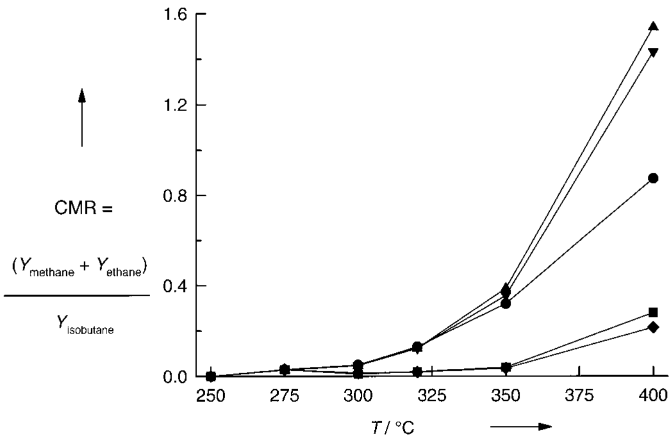

Figure 4. Temperature dependence of the cracking mechanism ratio (CMR) value during the conversion of methylcyclohexane on H-ZSM-5 catalysts with 0 (●), 0.001 (▲), 0.01 (▼), 0.2 (■), and 1.0 (◆) wt% of palladium.

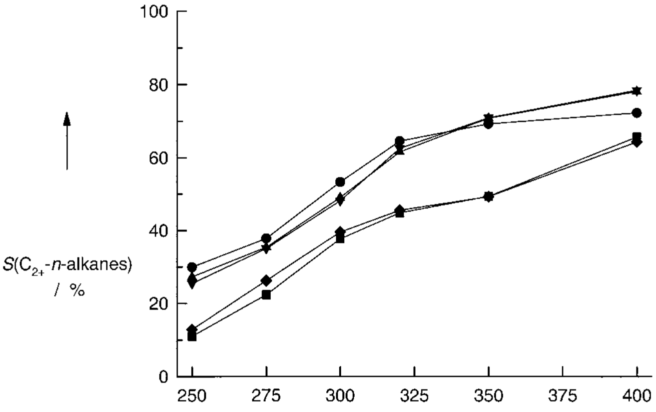

Figure 3. Temperature dependence of the selectivity to n-alkanes with two and more carbon atoms (S(C_{2+}-n-alkanes)) during the conversion of methylcyclohexane on H-ZSM-5 catalysts with 0 (●), 0.001 (▲), 0.01 (▼), 0.2 (■), and 1.0 (◆) wt% of palladium.

ions versus classical β-scission of carbenium ions (through the bimolecular or bifunctional mechanism), increase with increasing temperature. Similar trends have already been observed by Haag and Dessau[8] during cracking of hexane isomers on acidic zeolites and interpreted in terms of a high activation energy of the nonclassical cracking route. On typically bifunctional catalysts, this nonclassical cracking occurs only to a small extent. The dehydrogenation of methylcyclohexane is now efficiently catalyzed, hence there is a relatively high steady-state concentration of unsaturated hydrocarbons (for example, methylcyclohexenes), which are much more strongly adsorbed on the acidic sites than the saturated compounds. This results in a relatively high concentration of classical carbenium ions and a low concentration of nonclassical carbonium ions, hence the classical β-scission clearly dominates ($\text{CMR}_{400\,^{\circ}\text{C}} \cong 0.3$, Table 1). The β-scission can also take place on monofunctional acidic catalysts. However, the carbenium ions have to form in a sterically demanding, bimolecular hydride transfer (Scheme 1 a, bottom). Thus, bimolecular classical cracking is, especially under sterical constraints as in the medium-pore zeolite ZSM-5, accompanied by nonclassical cracking, indicated by a significantly higher CMR value (0.9 at 400 °C). Even higher values (approximately 1.5 at 400 °C) could be observed on H-ZSM-5 zeolites with 10 or 100 ppm of palladium, which indicates that nonclassical Haag–Dessau cracking is very much favored on these catalysts.

Of course, it would be desirable to perform such comparisons of the catalytic properties of various zeolites at low conversion. However, because of its higher activation energy, Haag–Dessau cracking becomes only significant at temperatures around 400 °C, and at these high temperatures low conversions would have been very difficult to achieve, even

Table 1. Conversion of methylcyclohexane at 400 °C on various H-ZSM-5 catalysts with different weight contents of Pd or Pt.

	0 ppm Pd	10 ppm Pd	100 ppm Pd	0.2 % Pd	1.0 % Pd	0.4 % Pt
$X_{\text{M-CHx}}$ [%]	100	100	99.8	100	100	100
Y_{Me} [%]	3.9	5.0	3.5	3.5	2.5	3.5
Y_{Et} [%]	10.4	15.4	12.3	6.1	4.5	6.0
Y_{Pr} [%]	48.6	51.7	51.5	47.8	47.0	48.5
$Y_{n\text{Bu}}$ [%]	12.4	10.6	13.7	12.6	12.7	13.1
$Y_{n\text{Pn}}$ [%]	1.0	0.5	0.9	0.2	0.2	0.3
$Y_{\text{C}_{2+}\text{-}n\text{-alkanes}}$ [%]	72.4	78.2	78.4	66.7	64.4	67.9
$Y_{\text{isoalkanes}}$ [%]	22.4	15.9	17.7	29.8	33.1	28.6
$Y_{\text{cycloalkanes}}$ [%]	0.0	0.0	0.1	0.0	0.0	0.0
$Y_{\text{aromatics}}$ [%]	1.3	0.9	0.3	0.0	0.0	0.0
CMR	0.86	1.54	1.44	0.33	0.22	0.34

with a drastic increase of the weight hourly space velocity (WHSV).

Tentatively, we attribute the prevalence of Haag–Dessau cracking on the catalysts with small amounts of palladium to the lack of an efficient formation mechanism for carbenium ions: On the one hand, there are not enough metal sites to dehydrogenate methylcyclohexane at a sufficiently high rate for the bifunctional mechanism to proceed. On the other hand, the number of metal sites suffices for a reasonably fast hydrogenation of the reaction products. This impedes the hydride transfer and, therefore, the classical cracking mechanism. This explanation is supported by the fact that, at the high partial pressure of hydrogen applied (6 MPa), hydrogenation should be favored over dehydrogenation. Hence, the formation of carbenium ions through both classical mechanisms is hindered.[11] Conversely, Haag–Dessau cracking is favored by a higher number of free acidic sites, which becomes especially visible at the high temperatures and with the pronounced spatial constraints which promote this mechanism.

A significantly higher proportion of nonclassical cracking on the catalysts with 10 or 100 ppm of palladium is in line with the maxima of the yields of C_{2+}-n-alkanes and methane, as well as with the minimum of the yield of isoalkanes (Figure 5 and Table 1). A rival mechanism for the formation of methane and ethane by hydrogenolysis on the metal[11] can, in all probability, be ruled out, because if it were operative the yields of methane and ethane would be expected to increase with increasing palladium content. In addition, the fact that the molar amount of the metal is important, but not its nature (Figure 2 and Table 1, 0.4 wt% Pt corresponds to about the same amount of metal as 0.2 wt% Pd), represents independent evidence against a contribution of hydrogenolysis under the reaction conditions applied here.

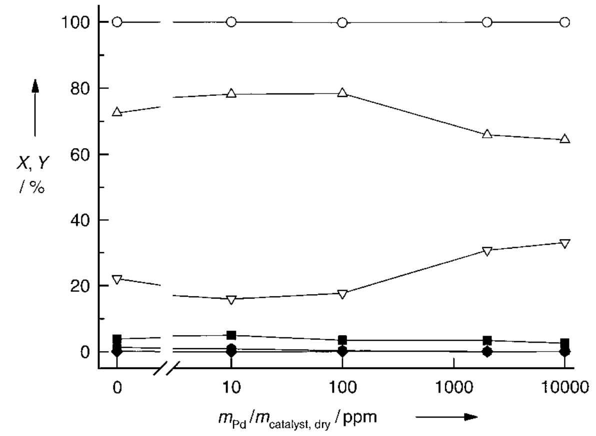

Figure 5. Effect of the palladium content on the conversion of methylcyclohexane on Pd/H-ZSM-5 catalysts at 400 °C. X: conversion, Y: yield. ○: X(M-CHx), △: Y(C_{2+}-n-alkanes), ▽: Y(isoalkanes), ■: Y(methane), ◆: Y(cycloalkanes), ⬢ : Y(aromatics).

In conclusion during the conversion of methylcyclohexane, maximal yields of n-alkanes with two and more carbon atoms, which are very desirable components for a synthetic steam-cracker feedstock, are not obtained on monofunctional acidic or on typically bifunctional catalysts, but on Pd/H-ZSM-5 zeolites with very small contents of noble metal in the range of approximately 10–100 ppm (approximately 78% at 400 °C). Such catalysts can be classified neither as monofunctional nor as bifunctional but, in the light of the present study, they represent rather a new type of catalyst, which we refer to as Haag–Dessau catalysts because the salient feature of the cracking performance of these catalysts is an unusually high contribution of nonclassical Haag–Dessau cracking.

Experimental Section

Zeolite ZSM-5 ($n_{Al}/(n_{Si}+n_{Al})=4.8\%$, that is, $n_{Si}/n_{Al}=20$, crystal size: $1.5\times0.5\times0.5$ µm) was hydrothermally synthesized as previously reported.[12] After ion exchange with aqueous solutions of ammonium nitrate and palladium(II) or platinum(II) tetraamminochloride, the samples were pretreated successively in flows of N_2 (12 h), air (2 h), N_2 (1 h), and H_2 (7 h) at 400 °C. This yielded catalysts with 0 (<90), 10 (<90), 100 (92), 2.0×10^3 (2.0×10^3), and 10×10^3 (10×10^3) ppm of palladium and 3.7×10^3 (4.0×10^3) ppm of platinum (referenced to the dry catalyst; the values given are calculated from the amount of metal salt used and in parentheses are the analytical values obtained by atomic emission spectroscopy with inductively coupled plasma (AES/ICP)). The catalytic experiments were performed in a stainless steel flow-type apparatus with a fixed-bed reactor. The mass of dry catalyst (particle size between 0.2 and 0.3 mm), the total pressure, the partial pressure of methylcyclohexane at the reactor inlet, and the WHSV were 500 mg, 6.0 MPa, 65 kPa, and 0.68 h^{-1}, respectively. Product analysis was achieved by capillary gas chromatography. No change of conversion, yields, or CMR value was observed due to the length of time on stream within 10 h. The experimental data given here were obtained after about 90 min on stream.

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