



## Isotopic studies on the dehydroalkylation of toluene with ethane

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### ABSTRACT

The complex network of alkylation, dealkylation, transalkylation, and isomerization reactions during the dehydroalkylation of toluene with ethane to ethyltoluenes on Pt/H-ZSM-5 has been investigated by studying separately the secondary hydroconversion reactions of several aromatics and by using deuterated toluene (Ph-CD<sub>3</sub>) as reactant for the dehydroalkylation reaction. Product analysis by GC-MS revealed that all aromatic products contained considerably fewer deuterium atoms than expected. This fact together with the appearance of large amounts of unlabeled toluene molecules at low toluene conversions and the presence of deuterium atoms within ethane molecules indicates that H/D exchange (via associative or dissociative adsorption of the reactants) is significantly faster than other reactions. The formation of 89% methane-d<sub>0</sub> and only 10% methane-d<sub>1</sub> can also be explained by H/D exchange and the interplay of total hydrogenolysis of aromatics and demethylation of toluene and/or ethyltoluene after H/D exchange.

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### 1. Introduction

The dehydroalkylation of aromatics with light alkanes is an example for the non-oxidative activation of alkanes. Using alkanes as alkylating agents for aromatics instead of the commonly used alkenes has the advantage that hydrogen can be recovered as valuable by-product due to the high molar hydrogen content of alkanes. The disadvantage is, however, that conversions are severely limited by thermodynamics. Hence, the mechanism of the dehydroalkylation of aromatics with alkanes is of major interest so that yields can be improved. In previous investigations, a reaction mechanism was proposed, involving first the dehydrogenation of the alkane to the alkene on the metal sites of the bifunctional catalyst and secondly the alkylation of the aromatic with the in situ formed alkene on the acid sites of the zeolite [1,2].

The reaction network including side reactions has been studied by changing the contact time during the dehydroalkylation of toluene with ethane [3] and the dehydroalkylation of benzene with ethane [4]. At low contact times and high times on stream, it is possible to obtain only ethyltoluene isomers and hydrogen as products of the dehydroalkylation of toluene with ethane. However, the conversions and hence yields of the products are low at low contact times. Increasing the contact time and therefore the conversions results in an initial increase in the yield of ethyltoluenes, but at higher conversions the selectivity to ethyltoluenes decreases

as the dehydroalkylation has to compete with the toluene disproportionation reaction as well as with secondary reactions of the products, ethyltoluene and hydrogen. With increasing conversion, C<sub>1</sub>–C<sub>4</sub> alkanes are also formed to a larger extent, as well as other aromatics including benzene, xylenes and ethylbenzene [3]. In that work, it has not been possible to elucidate the precise pathways of the formation of ethylbenzene, methane and propane.

In this article, we provide results of the separate hydroconversion of the reactant toluene as well as the products *p*-xylene and *p*-ethyltoluene in order to better understand secondary reactions. In addition, deuterated toluene (Ph-CD<sub>3</sub>) was used as reactant for tracing the pathway of the methyl group and further clarifying the reaction mechanism of the dehydroalkylation of toluene with ethane. In this way, ethylbenzene formation via hydrodealkylation of ethyltoluene should release deuterated methane, and toluene disproportionation should yield benzene-d<sub>0</sub> and xylene-d<sub>6</sub>. For isotopic studies of heterogeneously catalyzed reactions, substances labeled by <sup>13</sup>C or <sup>14</sup>C atoms are typically preferred because the original labeling position is generally maintained under reaction conditions [5–7]. Mechanistic studies with deuterated substances are often blamed for being less evident in comparison with <sup>13</sup>C or <sup>14</sup>C labeled compounds because H/D isotope exchange (proceeding often at higher rates than the conversion under study) can distort the labeling position to a greater or lesser extent. This disadvantage of deuterium labeling, however, can be used for probing the adsorption interactions between the catalyst and the reactants [8,9]. Usually, kinetic studies are performed to characterize the rate-determining step within a multitude of sequentially occurring reaction steps. Similarly, the observation of an intense

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H/D exchange at low (better would be zero) conversion can be used as an indication of fast interactions between the catalyst and the reactants. These interactions include the transport of reactants from the gaseous phase to the catalyst surface, associative or dissociative adsorption of the reactants, H/D transfer at surface sites as well as the desorption of the labeled molecules. Hence, if intense H/D exchange occurs at low conversion, the reaction under study cannot be diffusion-controlled. Thus, the application of deuterated compounds simultaneously allows to study both the reaction mechanism and sorption/diffusion interactions between reactants and catalyst. In addition, deuterated substances are typically 10–100 times cheaper than  $^{13}\text{C}$ -labeled compounds having similar isotope enrichments. It is the intention of the authors to demonstrate the suitability of isotopic studies using deuterated substances for the heterogeneously catalyzed dehydroalkylation of toluene with ethane.

## 2. Experimental

### 2.1. Catalyst preparation

Zeolite ZSM-5 was synthesized without organic template from Kieselsol (30 wt.%  $\text{SiO}_2$  in water, type VP-AC 4038, Bayer AG), sodium aluminate (54 wt.%  $\text{Al}_2\text{O}_3$ , 41 wt.%  $\text{Na}_2\text{O}$ , Riedel-de Haën), NaOH (>99 wt.%, Merck) and demineralized water, producing a synthesis gel with the molar composition  $60\text{SiO}_2:\text{Al}_2\text{O}_3:9\text{Na}_2\text{O}:2400\text{H}_2\text{O}$  [10]. Crystallization occurred within 5 days in a stainless-steel autoclave at  $160^\circ\text{C}$  under stirring at  $400\text{ min}^{-1}$ . The resulting zeolite was subjected to two consecutive ion exchange steps with an aqueous solution ( $1\text{ mol dm}^{-3}$ ) of  $\text{NH}_4\text{NO}_3$  (Fluka, 99.5%) at  $80^\circ\text{C}$ , each step lasting 4 h. At this stage, the zeolite was washed until it was nitrate-free. Thereafter, platinum ion exchange was carried out by adding an aqueous solution of  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  (Chempur, 55.63% Pt) drop-wise to a suspension of the ammonium ion-exchanged zeolite, under vigorous stirring, at room temperature, for 24 h. The elemental composition of the catalyst was determined by inductively coupled plasma atomic emission spectroscopy (Varian VISTA-MPX). The  $n_{\text{Si}}/n_{\text{Al}}$  and the amount of platinum were 28 and 0.4 wt.% (referenced to the mass of the dry catalyst), respectively.

### 2.2. Catalytic experiments

The zeolite powder was pressed without a binder, crushed, and size separated resulting in pellets with a particle size between 0.2 and 0.3 mm. The catalyst was activated in situ prior to starting the experiment. To achieve a high dispersion of the noble metal, the catalyst was first heated in flowing air ( $50\text{ cm}^3\text{ min}^{-1}$ ) at a rate of  $2^\circ\text{C min}^{-1}$  to a final temperature of  $300^\circ\text{C}$ , and held at this temperature for 22 h. After a purge with nitrogen for 30 min, the catalyst was heated during the reduction phase in flowing hydrogen ( $50\text{ cm}^3\text{ min}^{-1}$ ) at  $2^\circ\text{C min}^{-1}$  to  $350^\circ\text{C}$ , and held at this temperature for 22 h.

Catalytic experiments were performed in a flow-type apparatus with a fixed-bed reactor from stainless steel. Ethane (99.95 vol.%, Westfalen AG), nitrogen (99.999 vol.%, Westfalen AG), and for the hydrodealkylation experiments hydrogen (99.999 vol.%, Westfalen AG), were fed with an  $\dot{n}_{\text{nitrogen}}/\dot{n}_{\text{ethane}}$  ratio of approximately 5 through a saturator containing Chromosorb P-NAW (Macherey-Nagel) and the aromatic reactant (toluene (99.9%, Merck); deuterated toluene (isotopic purity by NMR: 97% Ph- $\text{CD}_3$ , DeuChem GmbH); *p*-xylene (>99%, Fluka); *p*-ethyltoluene (>97%, Merck)). Nitrogen was used as an internal standard but also to ensure that a relatively low  $\dot{n}_{\text{ethane}}/\dot{n}_{\text{toluene}}$  feed ratio of  $7 \pm 1$  could be achieved at the total pressure of 30 bar. The reaction temperature

was  $(350 \pm 2)^\circ\text{C}$ . Product analysis was achieved using an on-line sampling system, a capillary gas chromatograph and a CP-PoraPLOT Q column (Chrompack, length: 30 m, inner diameter: 0.32 mm, film thickness:  $20\ \mu\text{m}$ ). Two detectors in series were employed, namely, a thermal conductivity detector followed by a flame ionization detector. Correction factors for the two detectors were determined separately. With ethane as tie substance, the results from both detectors were combined. From molar flows, the selectivities of all products were calculated in %. The yields were determined from the selectivities and the toluene conversion.

During the experiments with deuterated toluene, integral product samples were collected using a cooling trap immersed in an acetone/dry ice bath ( $-78^\circ\text{C}$ ). In cases where gas samples were of interest for further analysis, a train of cooling traps was applied. The first cooling trap was immersed in an acetone/dry ice bath ( $-78^\circ\text{C}$ ) in order to trap all the aromatics. This was followed by two other cooling traps immersed in liquid nitrogen baths ( $-196^\circ\text{C}$ ) in order to trap light alkanes including methane. The reaction products were analyzed on an Agilent 6890N gas chromatograph coupled with mass detector (Agilent 5973) using a GasPro column (J&W Scientific, length: 60 m, inner diameter: 0.32 mm, heating rate:  $20\text{ K min}^{-1}$  starting from  $35^\circ\text{C}$  (retained for 3 min) to  $100^\circ\text{C}$  (retained for 3 min)). For gaseous products, the column was held at  $-10^\circ\text{C}$ . A comparative experiment for the alkylation of toluene- $\text{d}_3$  with methanol (99.7%, Riedel-de Haën,  $\dot{n}_{\text{methanol}}/\dot{n}_{\text{toluene}} = 1$ ) was carried out at  $420^\circ\text{C}$ , 1 bar ( $\dot{n}_{\text{nitrogen}} = 3\text{ dm}^3\text{ h}^{-1}$ ) and a WHSV of  $3\text{ h}^{-1}$ . The deuterium content of the hydrocarbons was calculated using a matrix method and a reference spectrum of the nondeuterated substance [11].

### 2.3. Computational methods

Density Functional Theory (DFT) calculations were carried out using Becke's three-parameter functional (B3) in combination with the Lee, Yang, and Parr (LYP) correlation functional [12,13]. The molecular geometries, energies and frequency analysis were calculated for the gas phase at the same B3LYP/6-31G\*\* (Jaguar version 7.0 program [14]) level of theory. Frequency analysis was used to obtain thermochemical parameters such as zero point energy (ZP), entropy (S), and Gibbs free energy ( $G^\circ$ ) at  $25^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Dehydroalkylation reaction

Table 1 shows in the second column the results of the dehydroalkylation of nondeuterated toluene with ethane. As catalyst, 0.4Pt/H-ZSM-5 was chosen so that the selectivity to methane is very high in order to facilitate mechanistic studies. Usually, the selectivity to methane is also higher at the beginning of the experiment [3], and this is why the data is given at relatively short time on stream (90 min). The second most important products after methane are the desired ethyltoluenes and hydrogen. The combined benzene and xylenes selectivity is about 18%. These products are generally thought to be formed by disproportionation of toluene. It has been observed earlier that the selectivities to the main aromatic products are similar at the beginning of the experiment and that the selectivity to the ethyltoluene isomers increases with increasing time on stream [15]. In the third column of Table 1, the results of the dehydroalkylation of deuterated toluene with ethane are given. The toluene conversion is slightly higher, and this can be explained by the lower WHSV of  $1.8\text{ h}^{-1}$  (as compared to  $2.3\text{ h}^{-1}$  for the nondeuterated toluene). The selectivities to the other products are also somewhat different from those observed during conversion of nondeuterated toluene, but in a similar range. The largest deviation

**Table 1**

Toluene dehydroalkylation (dehydroalk.) and toluene, *p*-xylene, *p*-ethyltoluene hydroconversion (hydroconv.) on 0.4Pt/H-ZSM-5 ( $n_{Si}/n_{Al}=28$ ) catalyst at 350 °C, 30 bar (make-up gas was nitrogen in all cases) and 90 min on stream. The dehydroalkylation reaction  $\dot{n}_{ethane}/\dot{n}_{toluene}$  feed ratio is 7.

Reaction	Toluene dehydroalkyl.	Toluene-d <sub>3</sub> dehydroalkyl.	Toluene hydroconv.	<i>p</i> -Xylene hydroconv.	<i>p</i> -Ethyltoluene hydroconv.
$P_{aromatic\ reactant}/bar$	1.0	1.0	1.0	0.2	0.2
$\dot{n}_{H_2}/\dot{n}_{aromatic\ reactant}$	–	–	0.8	3.0	3.0
$WHSV/h^{-1}$	2.3	1.8	0.69	0.14	0.14
$X_{aromatic\ feed}/\%$	10.7	13.7	5.3	11.3 <sup>a</sup>	99.8 <sup>a</sup>
$S_{hydrogen}/\%$	13.8	21.1	n.a. <sup>b</sup>	n.a. <sup>b</sup>	n.a. <sup>b</sup>
$S_{methane}/\%$	37.4	17.3	41.0	16.9	1.1
$S_{ethane}/\%$	n.a. <sup>b</sup>	n.a. <sup>b</sup>	0.8	2.0	42.6
$S_{propane}/\%$	7.0	4.7	2.6	3.7	d.l. <sup>c</sup>
$S_{benzene}/\%$	9.9	15.2	45.9	2.0	1.9
$S_{ethylbenzene}/\%$	3.1	3.9	d.l. <sup>c</sup>	d.l. <sup>c</sup>	d.l. <sup>c</sup>
$S_{toluene}/\%$	n.a. <sup>b</sup>	n.a. <sup>b</sup>	n.a. <sup>b</sup>	51.5	53.2
$S_{xylenes}/\%$	8.0	13.3	9.7	n.a. <sup>b</sup>	1.2
$S_{ethyltoluenes}/\%$	20.8	24.4	d.l. <sup>c</sup>	2.4	n.a. <sup>b</sup>
$S_{trimethylbenzenes}/\%$	d.l. <sup>c</sup>	d.l. <sup>c</sup>	d.l. <sup>c</sup>	21.8	d.l. <sup>c</sup>

<sup>a</sup> Isomerization of *p*-xylene and *p*-ethyltoluene was not included in the conversion.

<sup>b</sup> Not applicable as the species is the reactant.

<sup>c</sup> Below detection limit.

is observed for the selectivity to methane, but this value is very sensitive to time on stream, conversion and the precise reaction conditions. Thus, the results show that mechanistic considerations derived from the experiments with deuterated toluene should also be valid for the conversion of nondeuterated toluene. However, before we concentrate on the analysis of the deuterated reaction products, the discussion of the hydroconversion experiments will give a clearer picture of the mechanistic questions to be solved.

### 3.2. Hydroconversion experiments

For the hydroconversion experiments, model reaction mixtures were chosen in order to approximate reaction conditions for secondary reactions during the dehydroalkylation reaction, where only small amounts of hydrogen are formed as product, which is then available as reactant for secondary conversion of aromatics. Therefore, the hydroconversion experiments were carried out under mild conditions, i.e., only 2% H<sub>2</sub> in N<sub>2</sub> was fed to the reactor along with the saturator temperature set to appropriate partial pressures to approximate typical dehydroalkylation reaction conditions. Hence, the partial pressure was higher for toluene, which is a reactant of the dehydroalkylation reaction, than for *p*-xylene or *p*-ethyltoluene, which are products formed in lower amounts. The time-on-stream behavior of all catalysts was constant during hydroconversion experiments. Table 1 shows that the toluene conversion during hydroconversion of toluene was only 5%, about half of the conversion observed during the dehydroalkylation reaction. This demonstrates that the hydrodealkylation of toluene to benzene and methane is kinetically strongly hindered, even though thermodynamics predict equilibrium conversions between 90 and 100% [16]. During the hydroconversion of *p*-xylene, a higher conversion of about 11% was observed which might be explained by the lower partial pressure of the aromatic reactant and the lower WHSV. In Table 1, the conversion of *p*-xylene by isomerization is excluded, which appeared to be the dominating reaction. During the hydroconversion of *p*-ethyltoluene, essentially complete conversion, 99.8%, was achieved. This gives a good indication of the instability of ethyltoluenes in a hydrogen-containing atmosphere and explains the difficulties in achieving high conversion and selectivities during the dehydroalkylation of toluene with ethane. The main products split off the aromatic rings are methane during toluene and *p*-xylene hydroconversion and ethane during *p*-ethyltoluene hydroconversion. The strongly increased conversion during *p*-ethyltoluene hydroconversion could, therefore, be due to the presence of the ethyl group. Further implications of the

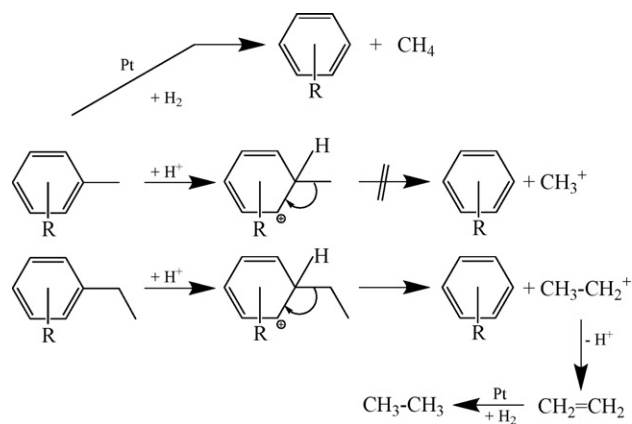
different reactions will be discussed separately in the following paragraphs.

During toluene hydroconversion, benzene and methane are the most abundant products with near equimolar selectivities of 46 and 41%, respectively (Table 1). This is a clear indication of the fact that toluene hydrodealkylation is the primary reaction for the formation of methane. The selectivity to xylenes is similar to that during the dehydroalkylation reaction. However, the yield of xylenes is lower due to the lower conversion. The lower yield to xylenes may be explained by competition of the toluene hydrodealkylation reaction (which is no longer a secondary reaction) with the toluene disproportionation reaction. Therefore, it appears as though the activity for the disproportionation reaction is reduced. Small amounts of ethane and propane are indicative for the catalyst being not highly active for hydroconversion of the aromatic ring to light alkanes under such mild conditions.

During the hydroconversion of *p*-xylene, *p*-xylene disproportionation also takes place to a large extent, forming toluene and trimethylbenzenes, with a selectivity of over 20% to the latter products. Toluene selectivity is much higher, over 50% (Table 1). This is presumably due to the hydrodealkylation of xylenes forming toluene and methane. A small amount of benzene is also observed. This may be due to secondary reactions of toluene, either by disproportionation or hydrodealkylation. Again, the activity of the catalyst for xylenes hydrodealkylation is high, whereas hydroconversion of the aromatic ring to light alkanes takes place to a smaller extent only (6% combined selectivity to ethane and propane). Interestingly, small amounts of ethyltoluenes are also formed during the hydroconversion of xylenes. This may be explained by xylenes transalkylation which would give toluene and ethyltoluenes.

During the hydrodealkylation of *p*-ethyltoluene, it is possible that either the ethyl or the methyl group is split off. Selectivity to ethane is about 43% (Table 1) and selectivity to toluene is about 53%. This indicates that the catalyst is highly active for the hydrodealkylation of the ethyl group in *p*-ethyltoluene which would yield ethane and toluene as products. In contrast, the catalyst seems inactive for hydrodealkylation of the methyl group yielding methane and ethylbenzene, with only 1% selectivity to methane and no detectable ethylbenzene. Small amounts of benzene and xylenes may result from the toluene disproportionation reaction, which is a secondary reaction here.

With regard to secondary reaction paths, several aspects have to be considered: in the presence of bifunctional catalysts, *hydrocracking*, i.e., cleavage with a bifunctional reaction mechanism including cracking on the acid sites and hydrogenation/dehydrogenation



**Scheme 1.** Possible pathways for the hydroconversion of alkylaromatics (R = H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>).

on the metal sites, is certainly preferred over *hydrogenolysis*, i.e., cleavage on the metal sites. Hydrocracking can also nicely explain the increased conversion of *p*-ethyltoluene as compared to the conversion of toluene and *p*-xylene (see above). One could consider a protonated aromatic reactant as intermediate (Scheme 1). Whereas splitting off an ethyl cation (which is subsequently rapidly deprotonated to ethene and hydrogenated to ethane over Pt) from protonated ethyltoluene is possible, no methyl cation can be split off protonated toluene or protonated ethyltoluene due to the low stability of this carbenium ion. Hence, the hydrodealkylation of ethyltoluenes to toluene and ethane is kinetically strongly favored, and this has also been observed by Serra et al. [17] on a Re/H-ZSM-5 catalyst and by Chizhov and Rabinovich [18] on a Mo/H-mordenite catalyst. However, on these catalysts at the higher reaction temperatures of 400–460 °C, small amounts of ethylbenzene were also detected in the product stream [17,18]. Chizhov and Rabinovich determined that the rates of splitting off isopropyl groups from cumene, ethyl groups from ethyltoluene, and methyl groups from pseudocumene (1,2,4-trimethylbenzene) had relative values of 19:7:1 [18].

These experimental findings can be confirmed by quantum chemical calculations. The probability of splitting off methyl or ethyl groups from ethyltoluene can be estimated from bond dissociation energies (*BDE*) calculated as difference of electronic energies  $\Delta E$  and difference of Gibbs free energies  $\Delta G$  of the various transition state complexes (Table 2). The values clearly reveal that splitting off the ethyl group is more favored than splitting off the methyl group. However, the bond dissociation energy for the ionic cleavage of ethyltoluene into ethylbenzene and the methyl cation is particularly high, thus supporting the mechanistic considerations in Scheme 1. Thus, whereas thermodynamic equilibrium prefers methane formation, the quantum chemical calculations of the activation energies for formation of the transition state complexes clearly show that ethyltoluene hydrodealkylation is strongly governed by kinetics.

Besides hydrocracking, hydrogenolysis reactions on the metal may also play a role, and an influence of the type of noble metal has previously been demonstrated with increased formation of methane and propane on the catalyst Pt/H-ZSM-5 as opposed to

**Table 3**

Molar composition of aromatic products of integral sample from cooling trap.

Reaction	Toluene-d <sub>3</sub> dehydroalkylation with ethane <sup>a</sup>	Toluene-d <sub>3</sub> alkylation with methanol <sup>b</sup>
Benzene/%	13.2	14.1
Ethylbenzene/%	4.6	0.5
<i>m,p</i> -Xylene/%	18.3	59.5
<i>o</i> -Xylene/%	5.7	17.1
Ethyltoluenes/%	49.6	2.3
Trimethylbenzenes/%	8.6	6.5

<sup>a</sup> Toluene dehydroalkylation with ethane ( $\dot{n}_{\text{ethane}}/\dot{n}_{\text{toluene}} = 7$ ) on 0.4Pt/H-ZSM-5 ( $n_{\text{Si}}/n_{\text{Al}} = 28$ ) at 350 °C and 30 bar.

<sup>b</sup> Toluene alkylation with methanol ( $\dot{n}_{\text{methanol}}/\dot{n}_{\text{toluene}} = 1$ ) on 0.4Pt/H-ZSM-5 ( $n_{\text{Si}}/n_{\text{Al}} = 28$ ) at 420 °C and 1 bar.

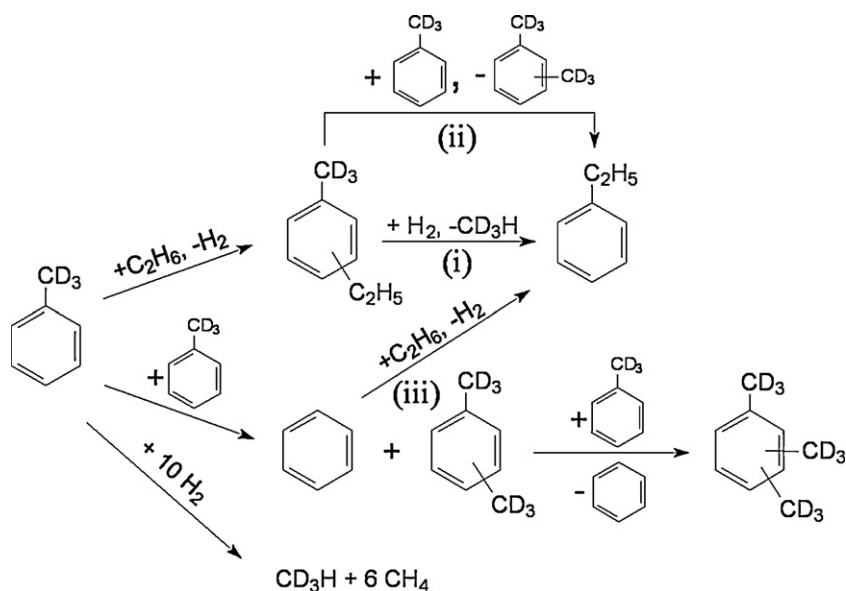
Pd/H-ZSM-5 [1]. Therefore, the two mechanisms probably proceed independently of each other. Depending on the reaction conditions, the metal and the metal dispersion as well as the reactant, hydrogenolysis or hydrocracking reactions might be prevailing. During the dehydroalkylation of toluene with ethane, hydrogenolysis reactions might be the dominant mechanism for hydrodealkylation of toluene, since the methyl cation is very unstable and since there is strong competition for acid sites with ethene formed from excess ethane. Under these conditions, hydrogenolysis of ethyltoluenes to ethylbenzene and methane is probably also taking place with an ethylbenzene selectivity of 3% (Table 1). However, during hydroconversion of ethyltoluene in the absence of ethane, hydrocracking to toluene and ethane should be favored.

### 3.3. Isotopic labeling and H/D exchange

As the previous sections showed, the conversion of alkylbenzenes on bifunctional zeolites represents a complex reaction network with many products, since in addition to the intended reaction, isomerization, transalkylation, and disproportionation reactions of the aromatic reactant as well as the aromatic products formed can occur [19]. For toluene dehydroalkylation with ethane, the ratio of toluene transalkylation vs. toluene dehydroalkylation is of particular importance because transalkylation reactions reduce the concentration of toluene and control thereby the yield of ethyltoluenes. To what extent toluene transalkylation takes place should be more obvious if the distribution of aromatic products obtained during the dehydroalkylation with ethane is compared with that of the toluene alkylation with methanol, a conventional alkylating agent, on the same Pt/H-ZSM-5 catalyst (Table 3). Obviously, the formation of the alkylation products ethyltoluenes and xylenes dominates during toluene (dehydro)alkylation with ethane and methanol, respectively. For both reactions, formation of benzene and trimethylbenzenes clearly points to disproportionation/transmethylation reactions of toluene. However, whereas the aromatic product contains 76.6% of the desired product when using the conventional alkylating agent methanol, only 49.6% of the desired product is obtained with the nonconventional alkylating agent ethane. Thus, transalkylation reactions occur to a larger extent during dehydroalkylation of toluene with ethane. From the mechanistic point of view, the formation of ethylbenzene can proceed via three routes: (i) hydrodealkylation of ethyl-

**Table 2**  
Bond dissociation energies and Gibbs free energies of alkyl elimination from ethyltoluenes.

Cleavage of ethyltoluenes to	Bond dissociation energy/kJ mol <sup>-1</sup>		Gibbs free energy of the transition state/kJ mol <sup>-1</sup>	
	Ionic	Radical	Ionic	Radical
Ph-CH <sub>3</sub> ( <sup>-</sup> or <sup>•</sup> ) + C <sub>2</sub> H <sub>5</sub> ( <sup>+</sup> or <sup>•</sup> )	1206	418	1097	337
Ph-C <sub>2</sub> H <sub>5</sub> ( <sup>-</sup> or <sup>•</sup> ) + CH <sub>3</sub> ( <sup>+</sup> or <sup>•</sup> )	1344	438	1273	364



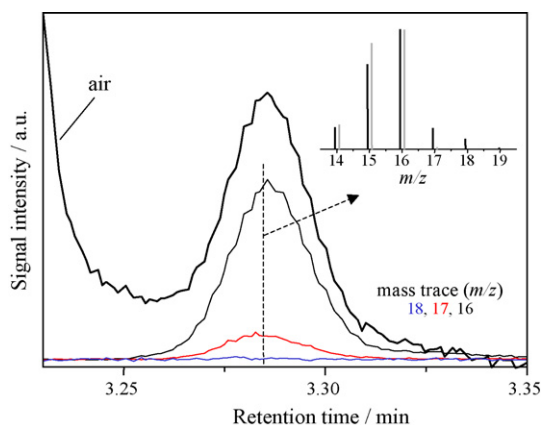
**Scheme 2.** Possible pathways for CD<sub>3</sub> groups during toluene dehydroalkylation with ethane.

toluenes, (ii) transmethylation of ethyltoluenes with toluene, and (iii) dehydroalkylation of benzene with ethane (Scheme 2). Using deuterated toluene (methyl group labeled, Ph-CD<sub>3</sub>) as reactant, toluene dehydroalkylation with ethane will yield ethyltoluene-d<sub>3</sub>. Consequently, the hydrodealkylation of ethyltoluene-d<sub>3</sub> to ethylbenzene should generate deuterated methane (Scheme 2). Therefore, the isotopic composition of methane should provide an indication of the extent of hydrodealkylation in comparison to the transmethylation and dehydroalkylation routes (ii) and (iii).

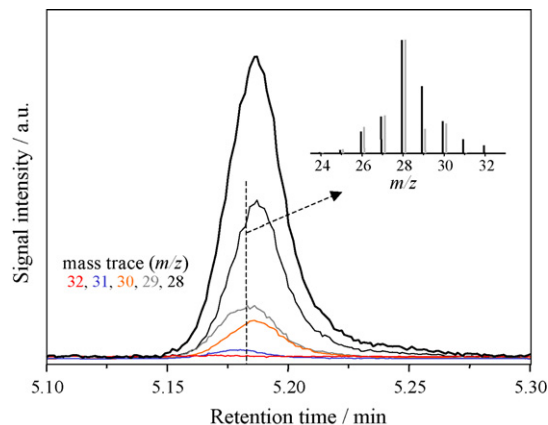
To obtain the isotopic composition of reaction products, GC–MS analysis is well established. However, undesired chromatographic separation of the isotopomers often complicates the evaluation of the GC peaks (see e.g. Fig. 1). To facilitate understanding, mass traces of main isotopomers are given in addition to the total ion current. As shown in Fig. 1, the chromatographic peak of methane reveals the formation of mainly methane-d<sub>0</sub> (89%) and a lower amount of methane-d<sub>1</sub> (10%). The appearance of CD<sub>3</sub>H (as expected by the hydrodealkylation of labeled toluene) cannot be confirmed, i.e., ethylbenzene formation via hydrodealkylation of ethyltoluenes (route (i)) seems to be marginal. Similar considerations should hold for toluene hydrodealkylation to benzene.

Surprisingly, the MS pattern of ethane (Fig. 2) clearly reveals the appearance of H/D isotope exchange between deuterated toluene and unlabeled ethane during toluene dehydroalkylation on Pt/H-ZSM-5. The presence of deuterium atoms within ethane molecules (1% ethane-d<sub>3</sub>, 4% ethane-d<sub>2</sub>, 15% ethane-d<sub>1</sub>, and 80% ethane-d<sub>0</sub>) points to associative or dissociative adsorption of both reactants, followed by H/D transfer between the adsorbed molecules as well as the desorption of the newly labeled molecules into the gaseous phase. Moreover, the occurrence of some multiple H/D isotope exchange (ethane-d<sub>2</sub> and ethane-d<sub>3</sub>) points to repeated interactions between the catalyst and both reactants even at a low degree of toluene conversion (~13%). Therefore, high rates of diffusion and adsorption processes can be assumed during toluene dehydroalkylation on Pt/H-ZSM-5.

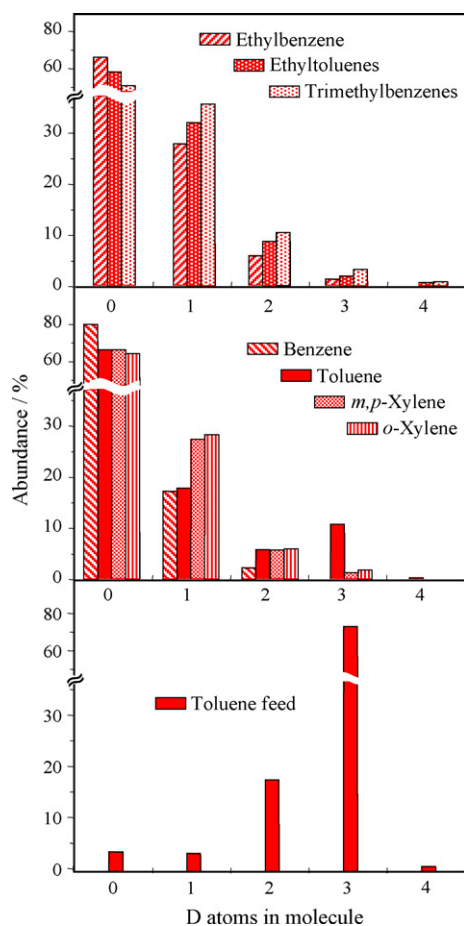
In the absence of intermolecular isotope exchange, none of the disproportionation/transmethylation reactions would change the labeling by the CD<sub>3</sub> groups fixed to the aromatic ring. Therefore, benzene-d<sub>0</sub>, toluene-d<sub>3</sub>, xylenes-d<sub>6</sub>, and trimethylbenzenes-d<sub>9</sub> were expected as isotopomeric products (Scheme 2). Product analysis by GC–MS revealed, however, that all of the methylated aromatics possess considerably fewer deuterium atoms than expected (Fig. 3 shows the signal of total ion current and the



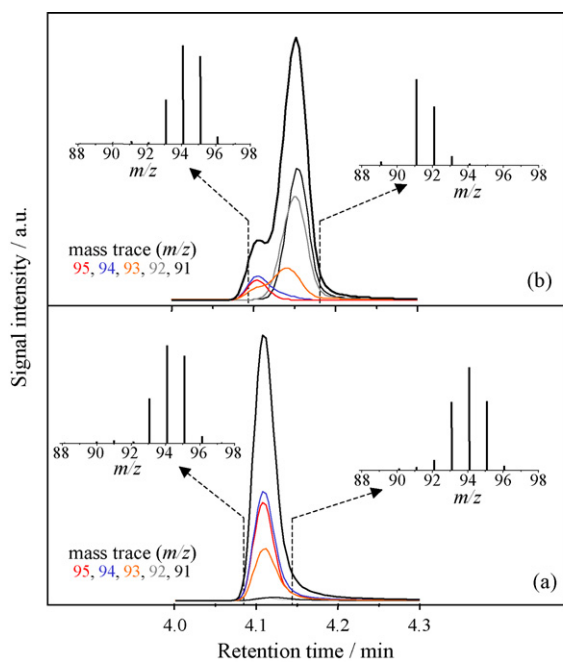
**Fig. 1.** GC–MS peak of methane after Ph-CD<sub>3</sub> dehydroalkylation with ethane-d<sub>0</sub> on 0.4Pt/H-ZSM-5 at 350 °C and 30 bar (insert: MS pattern of methane observed in comparison to nondeuterated methane (in gray)).



**Fig. 2.** GC–MS peak of ethane after Ph-CD<sub>3</sub> dehydroalkylation with ethane-d<sub>0</sub> on 0.4Pt/H-ZSM-5 at 350 °C and 30 bar (insert: MS pattern of ethane observed in comparison to nondeuterated ethane (in gray)).



**Fig. 3.** Deuterium distribution in the deuterated toluene feed and the aromatics obtained during Ph-CD<sub>3</sub> dehydroalkylation with ethane-d<sub>0</sub> on 0.4Pt/H-ZSM-5 at 350 °C and 30 bar.



**Fig. 4.** GC-MS peak of deuterated toluene (a) before and (b) after dehydroalkylation with ethane-d<sub>0</sub> on 0.4Pt/H-ZSM-5 at 350 °C and 30 bar (inserts: MS patterns of toluene observed at different retention times).

mass traces for toluene before and after dehydroalkylation with ethane-d<sub>0</sub>. Typically for chromatographic separation, isotopomers with a higher number of deuterium atoms are eluted at a shorter retention time than less deuterated ones. For CD<sub>3</sub>-labeled toluene as feed, mass spectra taken at the slopes of the GC peak indicate a uniform isotopic composition (Fig. 4a). On the other hand, toluene contained in the product mixture consists of several isotopomers which are partly separated by GC (Fig. 4b). Whereas the rising slope of the toluene peak points to the CD<sub>3</sub> labeling, the falling slope consists preferentially of toluene-d<sub>0</sub>. To explain the observed isotopic composition of toluene, the direct formation of unlabeled toluene from (unlabeled) ethane and/or intense H/D isotope exchange between toluene-d<sub>3</sub> and (unlabeled) ethane has to be assumed. Please note, by intramolecular H/D isotope exchange the labeling position within the toluene molecule, i.e., Ph-CD<sub>3</sub>, will become indefinite but the number of deuterium atoms remains. Although the build-up of toluene (and other aromatics) from ethane/ethene over Pt/H-ZSM-5 will certainly take place, the major content of toluene-d<sub>0</sub> and -d<sub>1</sub> (Fig. 4) is the consequence of a rapid H/D exchange between labeled toluene and unlabeled ethane molecules present in excess ( $\dot{n}_{\text{ethane}}/\dot{n}_{\text{toluene}} = 7$ ) (Fig. 2).

The increasing number of deuterium atoms within ethylbenzene < ethyltoluenes < trimethylbenzenes (upper part of Fig. 3) supports the assumption that H/D isotope exchange occurs simultaneously with toluene conversion. However, the appearance of a large amount of unlabeled toluene molecules at a low degree of toluene conversion (~13%), as well as the presence of deuterated ethane indicate that the rate of H/D exchange (via associative or dissociative adsorption of the reactants) is significantly higher than the rates of dehydroalkylation and transmethylation. Thus, H/D exchange proved to be an excellent tool to estimate the rate of adsorption/desorption as well as that of the preceding diffusion and showed that these reaction steps are not rate-determining for the toluene conversion under study. Due to the rapid H/D exchange the reason for the low deuterium content of the methane product remains unclear. On the one hand, the deuterium label of toluene and ethyltoluenes is probably to a large extent lost before secondary reactions such as hydrodealkylation can take place. On the other hand, total hydrogenolysis of toluene and the aromatics formed could also explain the formation of only small amounts of deuterated methane, since one molecule of toluene-d<sub>3</sub> would yield six molecules of methane-d<sub>0</sub> and just one molecule of methane-d<sub>3</sub> (Scheme 2). Other products of total hydrogenolysis could be ethane and propane (Table 1). Thus, as already mentioned in Section 3.2, both hydrocracking and hydrogenolysis of aromatics will probably take place, and there is not only one pathway for the formation of methane. Likewise, whereas it could be shown that hydrodemethanation of ethyltoluenes seems to be insignificant, both transmethylation of ethyltoluenes with toluene and dehydroalkylation of benzene with ethane are probably similarly important for the formation of ethylbenzene.

#### 4. Conclusions

Mechanistic studies with separate hydroconversion of aromatics and the use of deuterated toluene as reactant showed that the dehydroalkylation of toluene with ethane on bifunctional zeolite catalysts is not a simple reaction but involves a complex reaction network including disproportionation and transalkylation reactions of the toluene reactant and the aromatic products formed. Rapid H/D exchange leading to the formation of deuterated ethane proves that adsorption and desorption of reactants are significantly faster than the dehydroalkylation and the aromatics transformation reactions. The use of deuterated toluene could, therefore, not elucidate the pathway for the formation of secondary products such as methane and ethylbenzene.

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