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Selectivity Enhancement to the Exclusive Formation of Ethyltoluenes and Hydrogen During Dehydroalkylation of Toluene with Ethane

Seyed Alireza · Sadat Rezai · Yvonne Traa

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Abstract The dehydroalkylation of toluene with ethane to the isomeric ethyltoluenes was studied on 0.4Pt/H-ZSM-5 at varying contact times (1/WHSV). At a high contact time of 1.0 h, toluene disproportionation and hydrogenolysis reactions dominate, resulting in low selectivity to the desired ethyltoluenes via the alkylation reaction. However, at a low contact time of 0.12 h side reactions are eliminated, resulting in maximum selectivities to the kinetically favored ethyltoluenes and hydrogen. Results at high selectivities to ethyltoluenes provide significant insight into reaction pathways.

Keywords Dehydroalkylation · Aromatics alkylation · Ethyltoluenes · Pt/H-ZSM-5 · Alkane activation · Non-oxidative

1 Introduction

The production of alkyl aromatics as chemical intermediates represents large industrial processes. Estimates for current worldwide annual production capacities of ethylbenzene and cumene, the two most important chemicals produced by alkylation of aromatics, amount to 25×10^6 t a^{-1} and 10×10^6 t a^{-1}, respectively [1]. Conventional alkylating agents, including alkenes, alcohols and alkyl halides, have to be pre-synthesized via other processes, typically from an alkane feedstock. Alternatively, the direct alkylation of aromatics with *alkanes* may result in reduced costs and process intensification, since alkanes are much cheaper than other typical alkylating agents and are abundantly available in wet natural gas, and since pre-synthesis steps can be avoided. Whereas activity is a prerequisite for any catalyst, selectivity is a much more delicate parameter, and even small gains in selectivity are often very significant in successful processes. The selective activation of alkanes for environmentally sustainable development has been the focus of much research in homogeneous catalysis [2] as well as heterogeneous catalysis [3]. It is well known that high selectivities are generally obtained in homogeneous catalysis. However, there are usually other obstacles for large-scale realization of homogeneously catalyzed processes.

Whereas heterogeneously catalyzed processes are currently preferred for the production of chemical intermediates by alkylation, higher selectivities are desired. The importance of selectivity enhancement for alkylation reactions is evident in recent research using conventional alkylating agents where new materials or catalyst modifications resulted in cumene selectivities of >99% during the reaction of benzene with *propene* [4] or *isopropanol* [5] as well as older works on the alkylation of toluene with *ethene* where selectivities to ethyltoluenes and *p*-ethyltoluenes of 95% and 98% (the desired isomer relative to other ethyltoluene isomers) respectively have been reported [6]. Zeolites have especially gained more importance as selective catalysts for alkylation and disproportionation reactions of aromatics [7–9]. Recently, *propane* [10–13] and *ethane* [14–16] have been investigated as alkylating agents for benzene and toluene on metal-loaded (including Ga and platinum group metals) zeolite catalysts. The bifunctionality is required since an effective dehydroalkylation catalyst typically demands two types of active sites: a metal site for the dehydrogenation of the alkane and an acid site for the alkylation of the alkene intermediate with the aromatic molecule [17].

S. Alireza · S. Rezai · Y. Traa (✉)
Institute of Chemical Technology, University of Stuttgart,
70550 Stuttgart, Germany
e-mail: yvonne.traa@itc.uni-stuttgart.de

Although the alkylation of aromatics with alkanes is thermodynamically impaired [13–15], high conversions, even surpassing equilibrium, have been reported [13, 15]. However, these high conversions come at the expense of severe losses in selectivity. Typically, along with the desired products, light alkanes including methane, ethane or propane as well as other apparent alkylated or trans-alkylated products are observed. This is in contrast to conventional alkylation where the loss in selectivity is usually a result of polyalkylated aromatics formation and oligomerization of the alkylating agent, because of its high reactivity [18]. Using propane for benzene alkylation on a 0.3 Pt/H-ZSM−5 catalyst (0.3 wt.% Pt referenced to the mass of the dry catalyst, $n_{\mathrm{Si}}/n_{\mathrm{Al}} = 25$), Smirnov et al. [13] achieved a propane conversion of 45%; however, the combined molar selectivity toward propylbenzenes was only 5%, with selectivities of 30% to light alkanes and 20% to toluene and ethylbenzene. At a lower conversion of 0.5% on 0.02 Pt/H-ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 150$), the selectivity to the desired propylbenzenes was 85% (excluding hydrogen) with no light alkanes being detectable. Therefore, the authors concluded that losses in selectivity are a simultaneous result of propane cracking and propylbenzenes dealkylation [13]. Using a similar catalyst, 1.0 Pd/H-ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 20$), the more inert ethane as alkylating agent and toluene as substrate, Singer et al. [15] observed similar trends. At a toluene conversion of 27%, the molar selectivity to ethyltoluenes was only 29%. In fact, as conversion increased, the increase in methane selectivity was mirrored by a decrease in hydrogen selectivity, i.e., formation of methane creates a hydrogen sink, hence shifting the equilibrium toward ethyltoluenes. Cracking and dealkylation may be due to the nature of the catalyst, i.e., bifunctional catalysts of this type are well known to be also active for hydrocracking and hydrogenolysis of aromatics and alkanes [19–22], but the catalyst may only become active for such reactions with the formation of hydrogen, resulting in secondary reactions of hydrogen with the products or reactants.

In the present study, the direct gas-phase alkylation of toluene with ethane to form ethyltoluenes and hydrogen has been investigated as a model reaction for the non-oxidative activation of alkanes in a fixed-bed flow reactor. The focus was on improving selectivity to the desired ethyltoluenes and hydrogen, at the same time suppressing side reactions such as toluene disproportionation and hydrodealkylation as well as hydrocracking and hydrogenolysis reactions. The catalyst used was a bifunctional Pt/H-ZSM-5 catalyst with a relatively high activity and selectivity for the title reaction. During the Friedel-Crafts-type alkylation of toluene with *alkyl bromides*, using molar quantities of aluminum bromide, Brown and Jungk [23] succeeded in the elimination of the undesired toluene disproportionation reaction by reducing the contact time of the reactants with the catalyst by two orders of magnitude. It appears that the toluene disproportionation reaction, although a primary reaction, is kinetically less favored than the alkylation reaction, therefore disappearing at low contact times. Hence, the WHSV and thus the contact time were varied in this work during the alkylation of toluene with *ethane* in order to improve selectivity toward the title reaction to 100% and avoid the formation of byproducts.

2 Experimental Section

2.1 Catalyst Preparation

Zeolite ZSM-5 was synthesized without organic template from Kieselsol (30 wt.% SiO_2 in water, type VP-AC 4038, Bayer AG), sodium aluminate (54 wt.% Al_2O_3, 41 wt.% Na_2O, Riedel-de Haën), NaOH (>99 wt.%, Merck) and demineralized water, producing a synthesis gel with the molar composition 60 SiO_2:Al_2O_3:9 Na_2O:2400 H_2O [24]. Crystallization occurred within 5 days in a stainless-steel autoclave at 160 °C under stirring at 400 min^{-1}. The resulting zeolite was subjected to two consecutive ion exchange steps with an aqueous solution (1 mol dm^{-3}) of NH_4NO_3 (Fluka, 99.5%) at 80 °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 $Pt(NH_3)_4Cl_2$ (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 crystal size of the zeolite, as analyzed by scanning electron microscopy (CAM SCAN 44), was found to be approximately 3 μm. The elemental composition of the catalyst was determined by inductively coupled plasma atomic emission spectroscopy (Varian VISTA-MPX). The $n_{\mathrm{Si}}/n_{\mathrm{Al}}$ and the amount of platinum were 28 and 0.4 wt.% (referenced to the mass of the dry catalyst) respectively. It should be noted that the elemental analysis revealed a higher than usual amount of Na^+ ions after the completion of ammonium ion exchange, with an $\mathrm{n}_{\mathrm{Na}}/\mathrm{n}_{\mathrm{Al}}$ ratio of approximately 0.07. CHN analysis of the coked catalysts was accomplished using a Vario EL analyzer (Elementar Analysensysteme).

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 $cm^3\ min^{-1}$) at a rate of 2 °C min^{-1} to a final temperature of 300 °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 $cm^3\ min^{-1}$) at 2 °C min^{-1} to 350 °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) and nitrogen (99.999 vol.%, Westfalen AG) were fed with an $\dot{n}_{\mathrm{nitrogen}}/\dot{n}_{\mathrm{ethane}}$ ratio of approximately 5 through a toluene (>99.9%, Merck) saturator containing Chromosorb P-NAW (Macherey-Nagel). Nitrogen was used as an internal standard but also to ensure that a relatively low $\dot{n}_{\mathrm{ethane}}/\dot{n}_{\mathrm{toluene}}$ feed ratio of 7 ± 1 could be achieved at the high pressure applied (the optimum $\dot{n}_{\mathrm{ethane}}/\dot{n}_{\mathrm{toluene}}$ feed ratio is about 4 [14]). The reaction was carried out at a total pressure of 30 bar and a reaction temperature of (350 ± 2) °C. The WHSV (toluene and ethane) was varied between 1.0 h^{-1} and 8.2 h^{-1}. For the sake of simplicity, we define here *contact time* as the average time a differential element of the feed is in contact with catalyst from the top to the bottom of the catalyst bed. Mathematically, this may be represented as the reciprocal of the WHSV, thus, according to the WHSV range given contact times between 1.0 and 0.12 h will be discussed (cf. Table 1). This was achieved by changing the mass of catalyst from 0.85 to 0.10 g to ensure minimum change in the hydrodynamics of the system. Pressure drop as a result of the different catalyst masses was negligible. Each experiment was repeated with a fresh sample from the same catalyst batch. Experiments were repeated up to three times in order to ensure reproducibility of the results. The relative errors of different experiments were 4% and 6% for toluene and ethane conversions respectively. Product analysis was achieved using an on-line sampling system, a capillary gas chromatograph and a CP-PoraPLOT Q column (length: 30 m, inner diameter: 0.32 mm, film thickness: 20 µm, Chrompack). 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 the mass and molar flows, the selectivities of all products were calculated in mol%. The yields were determined from the selectivities and the toluene conversion. Gas samples were taken every hour. However, for the sake of clarity only every fifth point is given in the figures.

Table 1 Ethane and toluene conversions, product selectivities, and ratios of aromatic byproducts during the dehydroalkylation of toluene with ethane on 0.4Pt/H-ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 28$) with varying contact times (1/WHSV) at 350 °C, 30 bar and approximately 90 h on stream

Contact time (h)	1.0	0.59	0.33	0.25	0.12
WHSV (h^{-1})	1.0	1.7	3.3	4.0	8.2
$m_{\mathrm{dry\ catalyst}}$ (g)	0.85	0.50	0.26	0.21	0.10
X_{ethane} (%)	1.6	1.2	0.9	1.0	0.6
X_{toluene} (%)	16.3	13.0	6.5	6.3	3.6
$S_{\mathrm{ethyltoluenes}}$ (%)	27.4	35.8	58.8	52.9	60.5
S_{hydrogen} (%)	11.7	19.6	22.6	30.8	39.5
S_{methane} (%)	19.9	23.4	11.3	10.5	d.l.[a]
S_{propane} (%)	4.8	3.8	d.l.[a]	d.l.[a]	d.l.[a]
S_{benzene} (%)	15.9	8.0	5.0	4.1	d.l.[a]
S_{xylenes} (%)	17.2	6.5	d.l.[a]	d.l.[a]	d.l.[a]
$S_{\mathrm{ethylbenzene}}$ (%)	3.1	2.9	2.1	1.7	d.l.[a]
$\frac{S_{\mathrm{benzene}}}{S_{\mathrm{xylenes}}}$	0.9	1.2	>9[b]	>9[b]	–
$\frac{S_{\mathrm{benzene}}}{S_{\mathrm{ethylbenzene}}}$	5.1	2.8	2.4	2.4	–
$\frac{S_{\mathrm{xylenes}}}{S_{\mathrm{ethylbenzene}}}$	5.5	2.2	<0.2[b]	<0.2[b]	–
$\frac{X_{\mathrm{toluene,\ TOS} \approx 90\mathrm{h}}}{X_{\mathrm{toluene,\ TOS} \approx 2\mathrm{h}}}$	0.7	0.5	0.3	0.4	0.4
$\frac{S_{\mathrm{ethyltoluenes,\ TOS} \approx 90\mathrm{h}}}{S_{\mathrm{ethyltoluenes,\ TOS} \approx 2\mathrm{h}}}$	1.3	2.2	3.0	2.9	2.9

In addition, ratios of conversions and selectivities at 2 and 90 h on stream (TOS = time on stream) are given to indicate approximate (non-linear) changes between the beginning and end of each experiment

[a] Below detection limit

[b] Based on the detection limit

3 Results and Discussion

Figure 1 shows the time-on-stream behavior of the conversions of toluene and ethane over a 0.4Pt/H-ZSM-5 catalyst at varying contact times (CT), defined here as the reciprocal of WHSV. At a contact time of 0.12 h, the

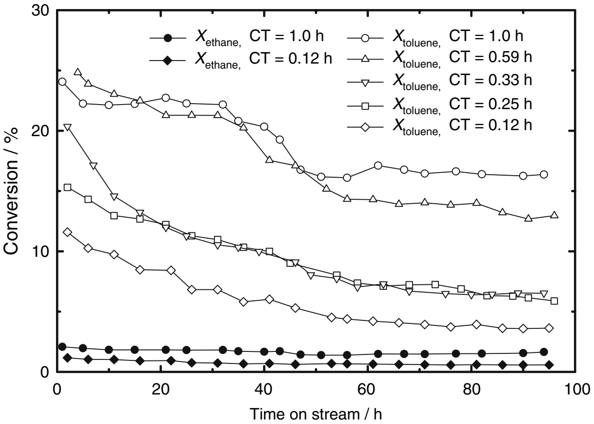

Fig. 1 Conversions of toluene and ethane on 0.4Pt/H-ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 28$) at 350 °C and 30 bar with varying contact times (CT) as a function of time on stream

toluene conversion at 2 h on stream is about 11%. Toluene conversion increases with increasing contact times. The conversions after 2 h on stream at contact times of 0.25 and 0.33 h are 15% and 20% respectively. However, beyond this point large increases in contact times result in insignificant improvements in conversions. At and above a contact time of 0.59 h, the toluene conversion at about 2 h on stream is about 25%. Ethane conversions are much lower than toluene conversions, since ethane is available in large excess. Still, a small increase in the ethane conversion can be observed with increasing contact time. Ethane conversion is about 1% at a contact time of 0.12 h, and is doubled at a contact time of 1.0 h. Ethane conversions stay almost constant during the entire run, whereas toluene conversions decrease strongly with increasing time on stream. However, after approximately 60 h on stream the toluene conversions level off and are thereafter relatively constant. The drop in toluene conversion varies according to the contact times. At a contact time of 1.0 h, the conversion at the end of run is about 0.7 times lower than the conversion after 2 h (cf. Table 1). The loss of conversion is higher as contact time decreases, and at a contact time of 0.12 h, the same conversion ratio is about 0.4. This variation appears not to be a result of different coking characteristics as contact time changes, since the carbon contents of all catalysts are around 6 wt.% independent of the contact time. The stronger deactivation tendency as compared to previous results (cf. [15]) can be explained by the nearly fivefold increase in time on stream and the considerably lower metal content of the catalyst which makes hydrogenation of coke precursors more difficult.

The time-on-stream behavior for product selectivities at the lowest contact time (0.12 h) is shown in mol% in Fig. 2. The selectivities of the desired ethyltoluene isomers and hydrogen are approximately 20% and 18%, respectively, after 2 h on stream. Methane selectivity is 36%, methane being the most abundant product at this short time on stream. Selectivities to other side products including propane, benzene, xylenes and ethylbenzene are low, between 3% and 10%. With increasing time on stream, the methane selectivity decreases sharply, and is below detection limit after approximately 60 h on stream. The selectivity of the other side products also decreases with time on stream, however, less rapidly. Benzene and xylenes are below detection limit after about 85 h on stream. As a result, the selectivity to the desired products increases with time on stream, and after approximately 85 h on stream ethyltoluenes and hydrogen are the only detectable products. Thus, the selectivity to the title reaction is 100%. This is due to coke selectivation and the short contact times, where the kinetically favored alkylation reaction is preferred over the disproportionation reaction.

According to the reaction stoichiometry, for the dehydroalkylation of toluene with ethane (cf. Fig. 3) it would be expected that the molar ratio of ethyltoluenes and hydrogen be approximately one to one. However, after about 90 h on stream the selectivity of ethyltoluenes is about 60% and that of hydrogen about 40%. The large differences may be a result of the fact that the hydrogen yields are determined using the thermal conductivity detector, and its correction factor is much smaller than correction factors for hydrocarbons determined from the flame ionization detector. From the evaluation of several mixtures of hydrogen and ethane by the thermal conductivity detector, it is estimated that the error in the hydrogen correction factor may be as much as 20%, whereas the same error is approximately 1%

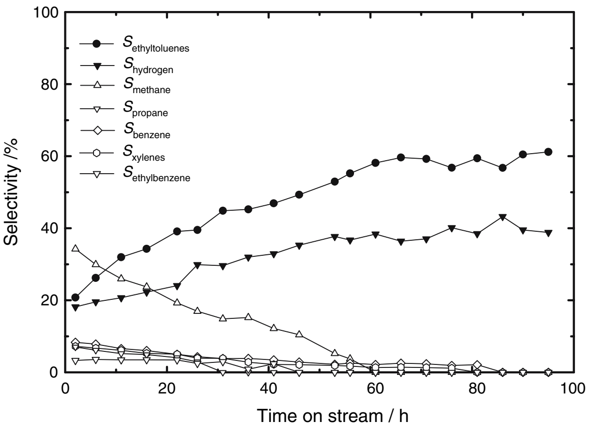

Fig. 2 Product selectivity on 0.4Pt/H-ZSM-5 ($n_{Si}/n_{Al} = 28$) at a contact time of 0.12 h, 350 °C and 30 bar as a function of time on stream

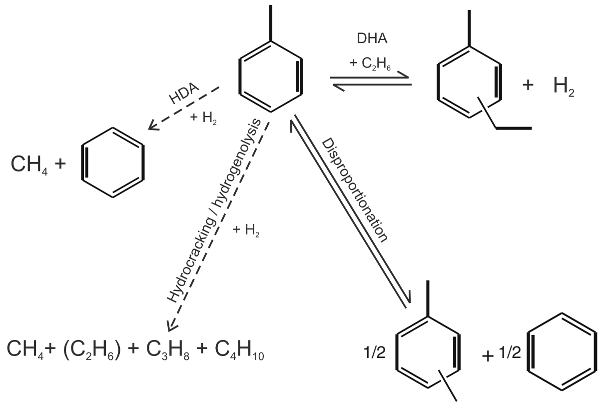

Fig. 3 Different reaction pathways possible during the dehydroalkylation of toluene with ethane. The solid arrows represent primary reactions, i.e., dehydroalkylation (DHA) of toluene with ethane yielding ethyltoluene isomers and hydrogen, and the disproportionation of toluene to xylenes and benzene. The dashed lines represent secondary reactions with hydrogen, including the hydrodealkylation (HDA) of toluene forming benzene and methane as well as hydrocracking/hydrogenolysis of toluene producing C_1 to C_4 alkanes. Ethane is given in parentheses as its formation from this reaction path can not be detected since it is a feed component

for ethane. Hence, hydrogen yields are much less accurate than hydrocarbon yields.

At all contact times, the initial selectivity to ethyltoluenes is approximately 20% (not shown). The selectivity increases with increasing time on stream. The trend of increasing selectivity is similar for all contact times, but at different rates depending on the contact time. At a contact time of 0.12 h, the selectivity to ethyltoluenes increases sharply, and is about 2.9 times higher at the end of the experiment than the selectivity after 2 h on stream (cf. Table 1). At the higher contact times, the increase in selectivity is less pronounced. For a contact time of 1.0 h, the selectivity to ethyltoluenes during 90 h on stream is essentially constant, with the ratio of the selectivity after 90 h on stream relative to 2 h on stream being approximately 1.3. The increase in selectivity, with a simultaneous decrease in conversion, means that the yield of ethyltoluenes remains almost constant throughout the experiment.

Similarly, at high contact times the drop in selectivity to the undesired side products is less severe. The methane selectivity after 2 h on stream is approximately 35% at all contact times on the 0.4Pt/H-ZSM-5 catalyst (not shown). At a contact time of 1.0 h, methane selectivity is high during the entire experiment, 32% after 2 h on stream (not shown), dropping to 20% after approximately 90 h on stream (cf. Table 1), whereas at a contact time of 0.12 h, methane selectivity drops to zero (see above).

On a 1.0Pd/H-ZSM-5 catalyst [15] and under similar reaction conditions, methane selectivity is about 10%. Methane is presumably formed mainly by hydrodealkylation of toluene (cf. Fig. 3), and Pt has been reported to be approximately five times more active than Pd at very similar selectivities for toluene hydrodealkylation at similar reaction conditions [19]. Hence, this could explain the higher methane selectivities observed with the Pt-containing catalyst. However, whereas Grenoble observed only methane and benzene as reaction products during toluene hydrodealkylation [19] the light products in our study also included propane and even trace amounts of C_4 hydrocarbons at high contact times. This can be explained by the higher acid strength and acid site concentration of zeolite H-ZSM-5 as compared to that of γ-alumina used as a support in the work of Grenoble [19]: Hence, light hydrocarbons may also be produced as a result of mild hydrocracking or hydrogenolysis of hydrocarbon species in our study (cf. Fig. 3). During the hydrocracking of methylcyclohexane on a similar Pd/H-ZSM-5 catalyst at 400 °C [25], but at much higher *hydrogen* pressure of 60 bar (resulting in complete conversion), similar products were observed, however with a lower contribution of methane and higher amounts of propane compared to the results presented here. However, due to the lower temperature, the low conversion and the lower hydrogen pressure applied here (compared to [25]) the catalyst is not active for hydrocracking at low contact times. However, with increasing conversion, more hydrogen is available for such secondary reactions and has a chance to undergo secondary reactions. Thus, the selectivities to light hydrocarbons increase with increasing contact time, whereas selectivity to hydrogen decreases since it is consumed (Table 1).

Table 1 also shows the selectivities to the aromatic side products formed during the reaction after 90 h on stream as well as certain selectivity ratios. At a contact time of 1.0 h, benzene and xylenes selectivities are about 16% and in the same range of the selectivity to the ethyltoluenes. However, the selectivity to these byproducts decreases with decreasing contact time to values much lower than the ones of the ethyltoluenes. Whereas benzene and xylenes are formed in very similar molar amounts at a contact time of 1.0 h, the selectivity to xylenes is significantly less than that to benzene at a contact time of 0.59 h. Furthermore, Table 1 shows that the selectivity to benzene is 5.0% and 4.1% at contact times of 0.33 and 0.25 h, respectively, in the absence of xylenes, resulting in benzene to xylenes ratios >9. At a contact time of 0.12 h, no aromatic side products can be detected any more. Although small deviations from unity of the $S_{\text{benzene}}/S_{\text{xylenes}}$ ratio may be expected and explained for example by dealkylation of xylenes [26], the total absence of xylenes at low contact times strongly suggests that other reaction mechanisms also account for benzene formation. We therefore suggest that, under conditions of *high contact time*, benzene is formed along with xylenes mainly from the disproportionation of toluene. However, at *low contact times* the disproportionation reaction appears to be not active, and this has been observed earlier during alkylation of toluene with ethene and ethyl bromide [23, 27–29]. Pore restrictions within the zeolite channels and the high $\dot{n}_{\text{ethane}}/\dot{n}_{\text{toluene}}$ ratio suppress the toluene disproportionation reaction requiring two toluene molecules as opposed to the alkylation reaction requiring only one [15]. At low contact times, benzene could be formed via the hydrodealkylation of toluene with hydrogen forming methane as a side product (cf. Fig. 3), as already discussed above. However, from the relatively low yields at low contact times it appears that this contribution is small compared to the disproportionation of toluene at high yields and high contact times. Thus, hydrodealkylation is presumably also taking place to a small extent at high contact times.

Ethylbenzene selectivities are also significant at high contact times; the ratio of benzene to ethylbenzene selectivities decreases with decreasing contact time. At a contact time of 1.0 h, the ratio is 5.1 decreasing to 2.4 at a contact time of 0.25 h, and after further reduction of contact time, both selectivities are below the detection limit. The relatively small ratio of benzene to ethylbenzene selectivities suggests that the dehydroalkylation of benzene with ethane is probably not the only possibility for the formation of ethylbenzene, as has been previously suggested in our work [15], as up to about 30% of the benzene formed would have to be alkylated to achieve such ratios. This is unlikely since less toluene is alkylated, even though its concentrations are much higher. Another possibility is the hydroisomerization of xylenes to ethylbenzene. The thermodynamics of this reaction favor ethylbenzene formation ($X_{\mathrm{equilibrium,\ 600K}} \approx 90\%$). However, as at low contact times ethylbenzene is formed in the absence of xylenes and as at higher contact times, which would facilitate formation of ethylbenzene by hydroisomerization, the ratio of xylenes to ethylbenzene selectivity (cf. Table 1) is much too high according to equilibrium, the contribution of this reaction pathway is probably also not too high. The third possibility for the formation of ethylbenzene is the hydrodemethylation of ethyltoluenes. Hydrodealkylation reactions could account for an excess of benzene to xylenes and ethylbenzene as well as for their selectivity ratio if one takes into account that more toluene is available than ethyltoluene. However, ethyltoluenes probably react with hydrogen rather under the formation of toluene and ethane. Hence, it is likely that different reactions contribute to the formation of ethylbenzene and the precise pathway could not be elucidated in this work.

Plotting the product yields as a function of toluene conversion at 90 h on stream (cf. Fig. 4), a maximum in ethyltoluenes yield is observed at a conversion of about 13% (equivalent to a contact time of 0.59 h, cf. Fig. 1). A maximum in the yield of ethyltoluenes may be a result of reactions in series, involving the primary products as reactants. The same maximum in ethyltoluene yield has also been previously observed during the alkylation of toluene with ethene [27, 28]. With ethene as alkylating agent, the maximum occurs at a lower contact time (approximately 0.3 h). Figure 4 also shows that the yields of xylenes and benzene gradually increase with increasing conversion. At low conversion, the benzene yield is higher than xylenes yield but with increasing conversions, both yields become similar. This shows again that at low conversions benzene is rather formed by hydrodemethylation of toluene. In addition, there is a steep increase in both yields, showing clearly that the disproportionation reaction starts becoming more dominant at high contact times. Yields of methane increase steadily with a maximum value of about 3.5% at high conversion. The fact that the methane selectivity is higher than the selectivity to benzene at contact times of 0.33 and 0.25 h (cf. Table 1) shows that methane must also be formed by total hydrogenolysis of toluene or hydrocracking (cf. Fig. 3) or other hydrodealkylation reactions.

Figure 5 represents the ratios of the selectivities of *m*-ethyltoluene to *p*-ethyltoluene after 2 h on stream and at the end of each experiment as a function of contact time. The bulkiest isomer, *o*-ethyltoluene, was typically observed in trace amounts only, with a maximum amount of less than 2% of the total amount of the ethyltoluene isomers. The low yields of *o*-ethyltoluene may be ascribed to it being too bulky to form inside the channels of the zeolite, where the primary reaction takes place. Due to the extra-framework Na^+ ions present within the channels of the 0.4Pt/H-ZSM-5 catalyst, the pore size of the channels is slightly reduced. Therefore, *o*-ethyltoluene may exclusively be formed on the external surface even at the highest contact times in this study, thus giving rise to smaller relative *o*-ethyltoluene selectivities than previously observed [14]. After 2 h on stream and at the shortest

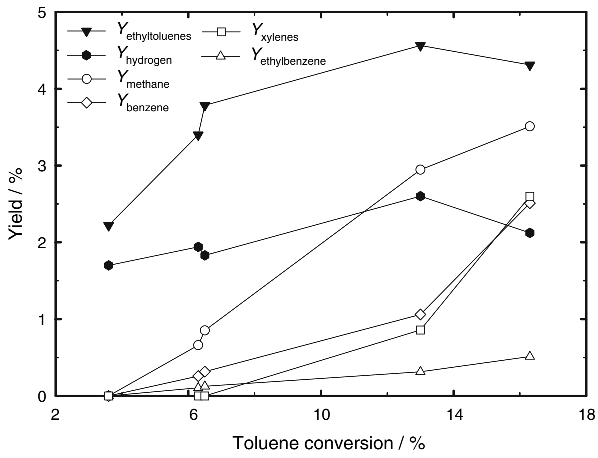

Fig. 4 Product yields on 0.4Pt/H-ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 28$) at 350 °C, 30 bar and 90 h on stream as a function of toluene conversion at different contact times

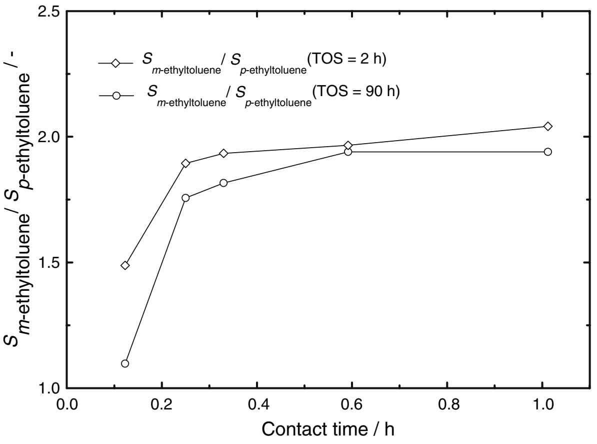

Fig. 5 Ratios of *m*-ethyltoluene to *p*-ethyltoluene selectivities on 0.4Pt/H-ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 28$) at 350 °C, 30 bar and 2 or 90 h on stream (TOS = time on stream) as a function of contact time

contact time of 0.12 h, the meta- to para-isomer ratio is about 1.5, increasing to 2 and staying at this value at higher contact times. After 90 h on stream at a contact time of 0.12 h, the ratio of the selectivities of *m*- to *p*-ethyltoluene is 1.1, increasing to a value of about 1.9 at higher contact times. The higher amount of *p*-ethyltoluene at low contact times has been attributed to primary formation of *p*-ethyltoluene, with subsequent isomerization to *m*-ethyltoluene during the alkylation of toluene with ethene on an H-ZSM-5 catalyst; the isomerization reaction can only take place to a small extent at low contact times [28]. The increase in para-selectivity with increasing time on stream has been explained either by enhanced diffusion rates of the slimmer para-isomer compared to the bulkier meta-isomer due to the narrowing of pores by coke deposition [6], by the deactivation of acidic sites responsible for the isomerization reaction [28], or by decreasing “effective” space time or contact time as a result of decreasing number of acid sites due to deactivation during the reaction, which increases the para-selectivity since the para-isomer is a primary product [27]. During the dehydroalkylation of toluene with ethane it is conceivable that interplay of all explanations may result in improvements. The decreasing effective contact time is also the reason for the increasing selectivity to ethyltoluenes with increasing time on stream (cf. Fig. 2), since the alkylation reaction is favored over the disproportionation reaction at low contact times.

4 Conclusions

The dehydroalkylation of toluene with ethane is possible on a Pt/H-ZSM-5 catalyst at a moderate temperature of 350 °C and a pressure of 30 bar. With increasing time on stream, conversions decrease but the yield of ethyltoluenes remains almost constant as a result of an increase in selectivity. The desired products, namely ethyltoluene and hydrogen, are formed exclusively at low contact times and high times on stream. The results provide significant insight into reaction pathways. At low contact times, the conversions and hence yields of the products are low. 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_1 to C_4 alkanes are also formed to a larger extent, as well as other aromatics including benzene, xylenes and ethylbenzene. A maximum yield of ethyltoluenes is observed at a conversion of 13% at 90 h on stream. It is suggested that this maximum is a result of secondary reactions of ethyltoluenes.

The fact that, at a low contact time, a selectivity of 100 % to the title reaction can be achieved, is the first step towards the industrial realization of the non-oxidative alkane activation. The second step could then be further improvement of the conversion, maintaining the high selectivity, e.g., by using a recycle or a membrane reactor.

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References

1. Ernst S, Petzny W (2005) In: eds. Dittmeyer R, Keim W, Kreysa G, Oberholz A (eds) Chemical technology, processes and products, vol 4, ch. 3. Wiley-VCH, Weinheim
2. Labinger JA, Bercaw JE (2002) Nature 417:507
3. Taniewski M (2006) Chem Eng Technol 29:1397
4. Corma A, Diaz-Cabañas MJ, Jordá JL, Martínez C, Moliner M (2006) Nature 443:842
5. Xiao FS, Wang L, Yin C, Lin K, Di Y, Li J, Xu R, Su DS, Schlögl R, Yokoi T, Tatsumi T (2006) Angew Chem Int Ed 45:3090
6. Kaeding WW, Young LB, Chu CC (1984) J Catal 89:267
7. Tsai T-C, Liu S-B, Wang I (1999) Appl Catal A 181:355
8. Čejka J, Wichterlová B (2002) Catal Rev - Sci Eng 44:375
9. Perego C, Ingallina P (2004) Green Chem 6:274
10. Bigey C, Su BL (2004) J Mol Catal A: Chem 209:179
11. Todorova S, Su BL (2004) Catal Today 93–95:417
12. Abasov SI, Babayeva FA, Zarbaliyev RR, Abbasova GG, Tagiyev DB, Rustamov MI (2003) Appl Catal A 251:267
13. Smirnov AV, Mazin EV, Yuschenko VV, Knyazeva EE, Nesterenko SN, Ivanova II, Galperin L, Jensen R, Bradley S (2000) J Catal 194:266
14. Sealy S, Traa Y (2005) Appl Catal A 294:273
15. Singer D, Sadat Rezai SA, Sealy S, Traa Y (2007) Ind Eng Chem Res 46:395
16. Kato S, Nakagawa K, Ikenaga N, Suzuki T (2001) Catal Lett 73:175
17. Caeiro G, Carvalho RH, Wang X, Lemos MANDA, Lemos F, Guisnet M, Ramôa Ribeiro F (2006) J Mol Catal A: Chem 255:131
18. Degnan TF Jr, Smith CM, Venkat CR (2001) Appl Catal A 221:283
19. Grenoble DC (1979) J Catal 56:32
20. Grenoble DC (1979) J Catal 56:40
21. Hoang-Van C, Villemin BL, Teichner SJ (1987) J Catal 105:469
22. Sinfelt JH (1970) Catal Rev - Sci Eng 3:175
23. Brown HC, Jungk H (1956) J Am Chem Soc 78:2182
24. Ernst S, Weitkamp J (1991) Chem Ing Tech 63:748
25. Weitkamp J, Raichle A, Traa Y (2001) Appl Catal A 222:277
26. Meshram NR, Hegde SG, Kulkarni SB, Ratnasamy P (1983) Appl Catal 8:359
27. Engelhardt J, Kalló D, Zsinka I (1992) J Catal 135:321
28. Lónyi F, Engelhardt J, Kalló D (1991) Zeolites 11:169
29. Engelhardt J, Szabó M, Kalló D (1992) Zeolites 12:916