The Reaction Network in the Conversion of 1,2,4-Trimethylbenzene over HZSM-5

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A reaction network for the conversion of 1,2,4-trimethylbenzene [1,2,4-TMB] over HZSM-5 is proposed, based on product concentrations versus space time studies at 723 K. At conversion levels below 10% the rates of formation of 1,2,3- and 1,3,5-TMB reflect the catalyst's activity for the isomerization of 1,2,4-TMB; the isomer distributions in the xylene and tetramethylbenzene fraction are not thermodynamically controlled and thus represent valuable information on the selectivity of the catalyst. As expected, product distributions were affected by the level of conversion, and thus selectivities have to be compared at equal conversions.   © 1998 Academic Press

INTRODUCTION

The use of reactant and product alkylaromatics to probe the effective pore width of molecular sieves under catalytically relevant reaction conditions has been extensively reviewed (1). Isomerization and disproportionation reactions of 1,2,4-trimethylbenzene [1,2,4-TMB] are expected to be highly restricted inside the micropores of HZSM-5 due to the critical dimensions of the reactant, transition-state intermediates, and products. Although it is not clear if these reactions are totally restricted inside the micropores (1, 2), they are more likely to occur mainly at acid sites near or on the external surface of the zeolite crystal. Thus the transformation of 1,2,4-TMB is expected to be sensitive to properties of the external surface and has thus been suggested as an ideal test reaction to probe the effects of external surface modifications on HZSM-5 (2). This reaction may be able to monitor the activity of the external surface and the influence of poremouth narrowing. The shape selective (3) properties of ZSM-5 zeolites may be probed by monitoring shifts in the product distribution towards shape selective products, such as 1,2,4,5-tetramethylbenzene (2) and *p*-xylene.

Depending on the steric constraints experienced by a reaction inside the micropores, the activity of the catalyst in this reaction may be correlated with one of the properties mentioned above. For instance 1,2,4-TMB isomerizes to 1,3,5-trimethylbenzene [1,3,5-TMB]. The diffusion of 1,3,5-TMB inside the ZSM-5 pores, however, is highly restricted due to the molecular dimensions (4). Thus 1,3,5-TMB observed in the product stream of the 1,2,4-TMB reaction is formed to a large extent on the external surface and it has been proposed that the rate of formation of 1,3,5-TMB correlates with the external surface activity (2). The rate of product formation as observed at the reactor outlet is, however, not necessarily identical to the rate of isomerization reactions transforming 1,2,4-TMB into 1,3,5-TMB in the catalyst bed, and is therefore not directly related to the isomerization activity of the catalyst. More often than not, parallel reaction paths and/or secondary reactions form and/or consume a certain product, and therefore affect the rate of product formation while the actual isomerization rate is independent of that.

The rate of a particular reaction in a network having only parallel reactions, without two reactions forming the same product, can be simply determined from the rates of product formation. The determination of reaction rates becomes more difficult when the reaction scheme involves relatively fast secondary reactions or when a product can be formed via more than one reaction path. The relationship between the measured rates of product formation and the reaction rate of a particular reaction can, however, be determined from a knowledge of the reaction network.

Ko and Kuo (5) studied the conversion of 1,2,4-TMB over zeolite HY. The proposed reaction network included isomerization and disproportionation as primary reactions. The isomerization led to the simultaneous formation of 1,2,3-TMB and 1,3,5-TMB and the disproportionation produced all isomers of xylene and tetramethylbenzene [TeMB]. Toluene and pentamethylbenzenes were observed as secondary products. The consecutive consumption and/or formation of the primary products, xylenes, TMBs, and TeMBs, was proposed to occur via disproportionation and transalkylation reactions. While the isomerization of 1,2,4-TMB to 1,2,3-TMB and 1,3,5-TMB occurred via parallel reactions, 1,2,3-TMB isomerized consecutively into 1,2,4-TMB and 1,3,5-TMB. This suggests that in the

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reaction of 1,2,4-TMB the consecutive isomerization of 1,2,3-TMB directly into 1,3,5-TMB is negligibly slow. These findings are consistent with the work of Collins *et al.* (6) who used zeolite LaY at 623 K. They reported the relative rate constants for the isomerization between 1,2,3-TMB and 1,3,5-TMB to be an order of magnitude smaller than the rate constants for the isomerization between 1,2,4-TMB and 1,2,3-TMB or 1,2,4-TMB and 1,3,5-TMB.

Chao and Leu (7) converted 1,2,4-TMB over NaHY at 543–733 K. They reported that the relative rate of disproportionation and isomerization depended on the acidity of the catalyst and the reaction temperature. Gnep *et al.* (8) used the transformation of 1,2,4-TMB to characterise the pore structure of HY, HM, and HZSM-5. Over HZSM-5 no conversion was observed at 623 K and a WHSV of $0.1\,h^{-1}$. It was suggested that 1,2,4-TMB is too bulky to access the active sites inside the micropores or alternatively these reaction products are too bulky to leave the micropore system. Unfortunately the Si/Al ratio was not given. These findings are not consistent with previous work by the authors, who observed significant conversion of 1,2,4-TMB at 723 K and a WHSV of $0.6\,h^{-1}$ over HZSM-5 with a Si/Al ratio of 26 (2).

The aim of this paper is to determine the reaction network occurring when 1,2,4-TMB is converted over HZSM-5. This was done by using concentration versus space time data and analysing the relevant product distributions.

EXPERIMENTAL

ZSM-5 powder [Si/Al = 25, particle size = 0.5–1.5 μm] in the ammonia form was deposited onto washed quartz sand particles [200–400 μm] and loaded into a stainless-steel down-flow fixed-bed reactor. It was previously confirmed that the quartz sand was catalytically inert. The catalyst bed was packed between beds of 4 and 3 g washed quartz sand upstream and downstream respectively. Calcination was carried out at 773 K in air for at least 5 h. 1,2,4-TMB [purity >98%], was converted at $T = 723$ K and a 1,2,4-TMB partial pressure of 3.5 kPa. The WHSV was varied from 0.0086 to 36 h^{-1} by changing both the feed flow rate and the catalyst mass, thus achieving space times ranging from 1.7 to 7000 min. Reaction products were sampled after 240 min. time on stream when the reaction system was in pseudo-steady-state using evacuated glass ampoules (9). Product analysis was done by gas chromatography using a Supelcowax 10 fused silica capillary column [30 m × 0.2 mm] and a PONA column [50 m × 0.2 mm]. Cyclohexane of 99.5% purity was fed to the product stream as internal standard.

RESULTS AND DISCUSSION

The difference between the concentration of 1,2,4-TMB in the bulk gas phase and the concentration on the particle surface was estimated to be smaller than 0.1% for all experiments using the equation of Wakao and Funazkri (10). This shows that gas film diffusion limitations are negligible. The ratio of reactor to particle diameter was 33 and thus exceeded a ratio of 15 which is sufficient to obtain plug flow (11). The following criterion for axial dispersion was used (12):

$$L/d_p > 20n/Pe_p \ln(1/(1-x)), \qquad [1]$$

where L is the bed length [3 cm], d_p is the particle diameter [300 μm], and the reaction order n was assumed to be 1. For particle Reynolds numbers smaller than 1, a particle Peclet number of 0.5 has been suggested to be used in Eq. [1] (13). The particle Reynolds number in this work was between 0.02 and 0.24. For a conversion of $x = 0.9$ the above criterion yields

$$L/d_p = 100 > 92 = 20n/Pe_p \ln(1/(1-x)). \qquad [2]$$

In summary effects of mixing due to axial dispersion or non-plug-flow conditions on the product distribution are insignificant at conversions less than 90%.

Figures 1 and 2 show lumped product concentrations as a function of space time. Figure 1 magnifies the profiles between 0 and 1000 min, while Fig. 2 shows the entire space time range investigated. The trends of the individual components in the C_1–C_4 lump are shown in Fig. 3. The curves for the individual isomers within the other lumps had similar shapes and are not expanded.

Figure 1 shows that the slopes at the origin of all curves except for the one representing benzene were greater than zero. In a constant density system, the rates of product formation equal the slopes of curves in concentration versus space time plots, according to the mass balance for a plug-flow reactor (14). The initial rates of product formation were determined in the space time interval between 0 and 4 min and are listed in Table 1. For series reactions the time–concentration curve for the final product has a zero slope at low contact times, whereas for products which are formed in primary reactions the slope is greater than zero (14). According to this criterion the following appear to be primary products in this reacting system: the C_1–C_4 fraction, toluene, xylenes, 1,2,3-TMB, 1,3,5-TMB, and TeMB isomers, whereas benzene is clearly a secondary product.

Generally disproportionation is the only reaction mechanism of a pure methylaromatic feed which yields higher substituted rings as a primary product, while isomerization is the only reaction where the number of methyl groups remains constant in the primary product. Lower substituted methylaromatics can theoretically be formed via two reaction pathways, viz. disproportionation and dealkylation. Thus, except for toluene, C_2's, C_3's, and C_4's, the observed primary products can be ascribed to well-known, primary,
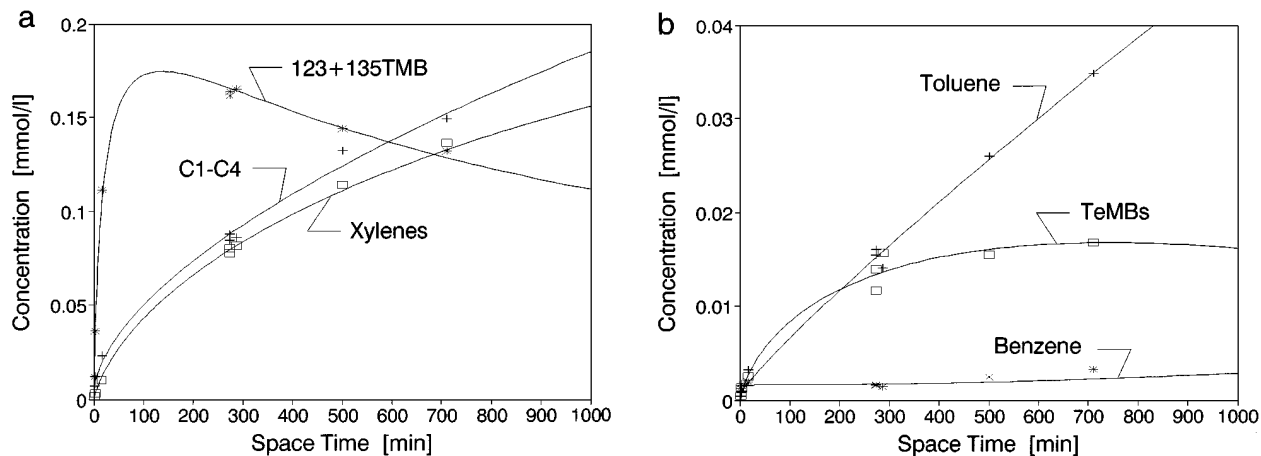
FIG. 1. Product concentrations during the conversion of 1,2,4-TMB over HZSM-5 for space times between 1.7 and 1000 $g_{cat}/(g_{feed}/min)$ [$T = 723$ K; $p_{1,2,4\text{-TMB, in}} = 3.5$ kPa; C_1–C_4, in mmol C/L].
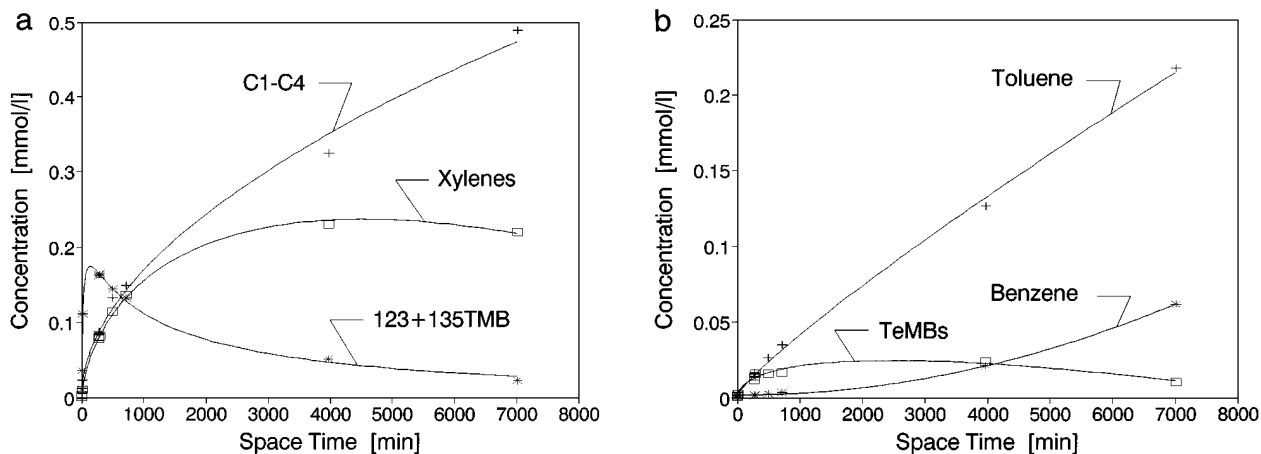

FIG. 2. Product concentrations during the conversion of 1,2,4-TMB over HZSM-5 for space times between 1.7 and 7000 $g_{cat}/(g_{feed}/min)$ [$T = 723$ K; $p_{1,2,4\text{-TMB, in}} = 3.5$ kPa; C_1–C_4, in mmol C/L].
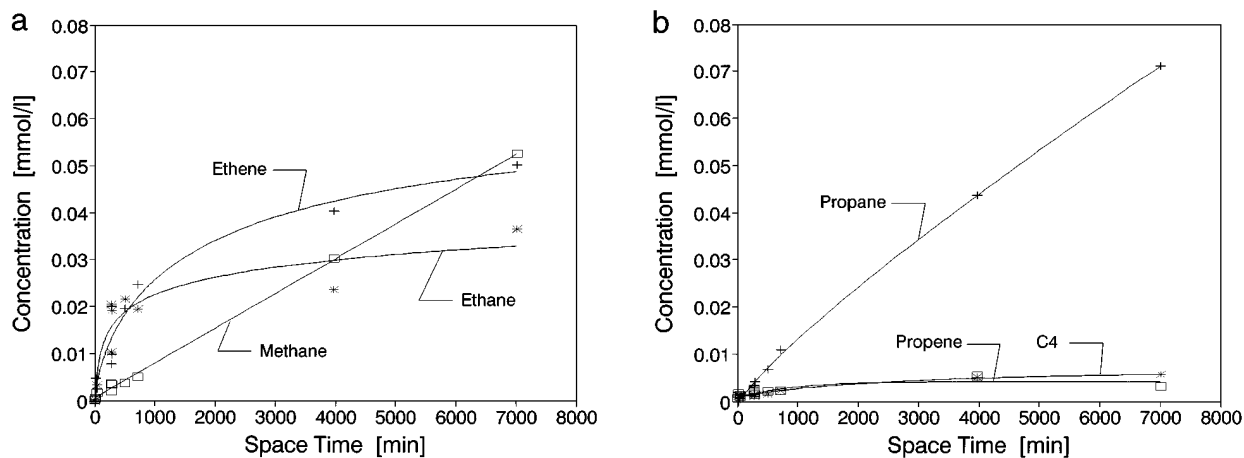

FIG. 3. Product concentrations of the C_1–C_4 fraction during the conversion of 1,2,4-TMB over HZSM-5 as a function of space time [$T = 723$ K; $p_{1,2,4\text{-TMB, in}} = 3.5$ kPa].

TABLE 1

Product Types and Initial Rates of Product Formation in the Conversion of 1,2,4-TMB over HZSM-5 As Determined from Space Time–Concentration Plots (1, Primary Product; 2, Secondary Product; S, Stable Product; U, Unstable Product)

Product	Product type, space time range		Rate (μmol/h/l)	Specific rate (μmol/h/g$_{cat}$)
	0–20 min	0–7000 min		
Methane	1 S	1 S	2.9	42
Ethene	1^d S	1^d S	4.3	62
Ethane	1^d S	1^d S	4.5	64
Propene	1^d S	1^d S	1.2	17
Propane	1^d S	1^d S	0.9	13
C$_4$	1^d S	1^d S	1.2	17
Benzene	2 S	2 S	0	0
Toluene^a	1^d S	1^d S	17	243
Xylenes	1 S	1 U	55	787
TMB's^b	1 S	1 U	620	8874
TeMB's^c	1 S	1 U	21	301

^{a} Observed as primary product; however, interpreted as secondary product.
^{b} Trimethylbenzenes.
^{c} Tetramethylbenzenes.
^{d} Pseudoprimary product.

acid-catalysed reactions of 1,2,4-TMB as follows:

(i) 1,2,3-TMB and 1,3,5-TMB — Isomerization
(ii) TeMBs — Disproportionation
(iii) Xylenes — Disproportionation, dealkylation
(iv) CH$_4$ — Dealkylation

It was found that the initial rate of formation of xylene was 2.6 times higher than that of TeMB (Table 1). If only disproportionation took place, the molar ratio of xylenes to TeMBs would have been 1. The surplus of xylenes observed thus indicates one or both of the following possibilities:

(i) TeMBs are trapped in the channel intersections as coke precursors or consumed in consecutive reactions. The formation of coke was indicated by a grey colour of the catalyst after reaction and a decreasing carbon balance with space time from near to 100% down to 90% (Fig. 4). The difference between the measured carbon balance and a carbon balance of ~100% may be interpreted as coke precursors retained on the catalyst surface. Since the slope at 0–4 min space time is different from zero, they appear to be primary products. This supports the assumption that TeMB isomers, which are also primary products, are retained as coke precursors inside the micropore volume.

(ii) Xylenes are formed via another parallel reaction path, such as demethylation of 1,2,4-TMB, which is thermodynamically favoured. However, the transformation of 1,2,4-TMB into methane and xylene requires hydrogen.

Since no hydrogen is fed, it would have to be supplied indirectly by hydrogen transfer reactions, which for example occur typically during the formation of coke or coke precursors. The concentration of methane increases linearly with space time, showing that the rate of methane formation remains constant. However, the rate of methane formation is not sufficient to match the surplus of xylenes present (Table 1).

The transformation of 1,2,4-TMB into ethane, ethene, propane, propene, and C$_4$'s is thermodynamically possible, and the alkanes are thermodynamically favoured relative to the alkenes. From a mechanistic point of view, however, it is difficult to see how these products could be formed from 1,2,4-TMB in a single step. It is therefore proposed that these pseudo-primary products, which are observed at very low space times, are actually formed in a series of consecutive cracking reactions. 1,2,4-TMB is proposed to undergo cracking of the aromatic ring, yielding methyloctenes, dimethylheptenes, and trimethylhexenes as intermediate primary products. These intermediates are subsequently cracked via β-scission to yield mainly C$_2$ and C$_3$ species. Due to the stabilising effect of the electronic structure of aromatic rings, cracking of aromatics is a slow reaction compared to the subsequent cracking of C$_9$-olefins. C$_9$-olefins are therefore converted before they can elute from the micropores and C$_2$–C$_4$ appear to be primary products. To form the observed products in the C$_2$–C$_4$ fraction, hydrogen transfer reactions would be necessary, which typically accompany coke formation.

All the curves representing (1,2,3-TMB + 1,3,5-TMB), TeMB, and the xylene isomers show a maximum (Fig. 2), indicating that these primary products are intermediates which are consumed in consecutive reactions (14). The concentration versus space time plots, however, for benzene,
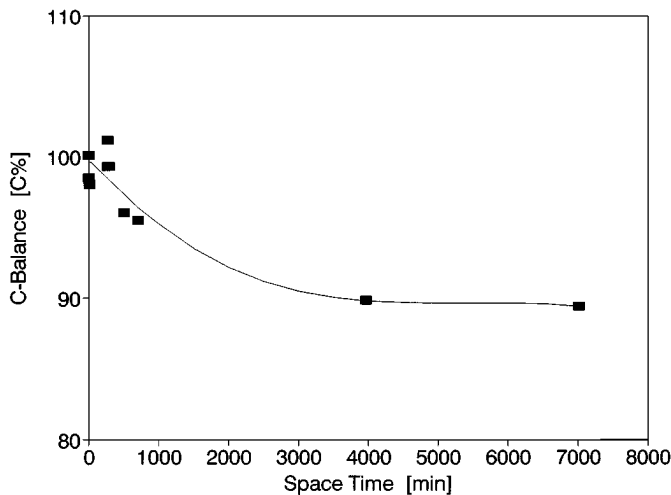
FIG. 4. Carbon balance during the conversion of 1,2,4-TMB over HZSM-5 as a function of space time, [$T = 723$ K; $p_{1,2,4\text{-TMB, in}} = 3.5$ kPa].

toluene (Fig. 2), and the C_1–C_4 fraction do not show maxima (Fig. 3) and are therefore classified as stable products. The categorization of various products with respect to primary and secondary, stable and unstable, is summarised in Table 1 on the basis of the concentration versus space time plots.

Isomerisation, disproportionation, dealkylation, and cracking are likely to occur not only as primary reactions of 1,2,4-TMB but also as secondary reactions of all methylaromatic products (Table 1). These secondary reactions would be consistent with the space time–concentration plots which indicate that TMBs, TeMBs, and xylenes are intermediates in the formation of toluene, benzene, and the C_1–C_4 fraction (Fig. 2). Transalkylation between benzene, toluene, xylenes, TMB's, and TeMB's to form methylaromatics are further possible secondary reactions.

In the case of toluene the initial rate of formation is clearly greater than zero (Table 1) indicating that it is a primary product. The formation of toluene as primary product in the absence of molecular hydrogen, may theoretically be achieved by monomolecular decomposition of 1,2,4-TMB into toluene and ethene. The equilibrium constant for this reaction, when reactant and products are in the ideal gas state, is $K_p = 0.14$, thus showing that this reaction is thermodynamically possible. The formation of toluene via this reaction path would, however, be accompanied by an equimolar formation of ethene. Since, the observed, initial rate of formation of ethene is only a quarter of the rate of toluene formation (Table 1) this speculative mechanistic route cannot fully explain the appearance of toluene as primary product. At this stage there is not enough evidence to prove or disprove the occurrence of the monomolecular decomposition of 1,2,4-TMB into toluene and ethene.

For the transformation of 1,2,4-TMB over zeolite Y, Ko *et al.* (5) proposed toluene to be a secondary product, formed by disproportionation of xylene. Although this proposal might by mechanistically correct, their lowest conversion was 10% and the curve had to be extrapolated in order to determine the slope at zero conversion, whereas in the present work space times yielding conversions down to 2% were investigated. There are two possible reasons why a secondary product may appear as an apparent primary product even at conversions as low as 2%. Either the contact time with the catalyst is not well defined or the consecutive reaction is very fast relative to the primary reaction. Both possibilities are reasonable explanations for the appearance of toluene as an apparent primary product as discussed below.

The actual contact time of molecules which are adsorbed into the zeolite micropores equals the time spent inside the micropore system plus the macroscopic residence time in the catalyst bed. Therefore, even at very short macroscopic contact times a certain fraction of the feed experiences a longer contact time due to adsorption

with the consequence that mechanistically secondary products may appear as pseudoprimary products in the reactor effluent.

The consecutive disproportionation of xylenes to form toluene is a reversible reaction. If this consecutive reaction is fast relative to the primary reactions, toluene might appear as an apparent primary product, as observed in the present work, without the complete consumption of the xylenes. Reactant, transition state intermediates and products occurring in the transformation of xylenes are smaller than in the transformation of 1,2,4-TMB. Therefore, the transformation of xylenes inside the micropores is sterically far less restricted than reactions of 1,2,4-TMB and a relatively fast formation of toluene by consecutive reactions of intermediate xylenes is feasible.

This work thus proposes that toluene is formed via consecutive reactions of xylene, viz. disproportionation, dealkylation, or transalkylation (Fig. 5) inside the zeolite pores. The possibility of a primary reaction of 1,2,4-TMB to form toluene has, however, still to be investigated. In the same way benzene is proposed to be a consecutive reaction product even though it is observed at the lowest space time investigated. Benzene is proposed to be formed by disproportionation, dealkylation, or transalkylation of toluene. It is not possible from the present data set to indicate which one of these possible mechanistic routes is dominant.

Figure 5 summarises the mechanistic pathways proposed above. The initial rates of formation listed in Table 1 were used to rank the primary products. The formation of 1,2,3-TMB and 1,3,5-TMB was an order of magnitude faster than the formation of TeMB's, xylenes, and the sum of the products in the C_1–C_4 fraction. Figure 6b shows that the isomerisation of 1,2,4-TMB only reaches equilibrium at conversion levels above 30%. Therefore, the initial rate of formation of 1,2,3-TMB and 1,3,5-TMB is not constrained thermodynamically. The equilibrium constants of the disproportionation reactions of 1,2,4-TMB, $K_{x,\mathrm{Dis}} = [i\text{-xylene}][i\text{-TeMB}][1,2,4\text{-TMB}]^{-2}$, range from $K_{x,\mathrm{Dis}}(450°C) = 0.054$ to $K_{x,\mathrm{Dis}}(450°C) = 0.34$ which is comparable to the equilibrium constant of the isomerization reaction of 1,2,4-TMB, $K_{x,\mathrm{Is}}(450°C) = [1,2,3\text{-TMB}][1,3,5\text{-TMB}][1,2,4\text{-TMB}]^{-2} = 0.048$. Because the equilibrium constants are similar and the rates of product formation via disproportionation are smaller than for the isomerization products (Table 1), the rate of xylene and TeMB formation is not thermodynamically constrained either at conversions below 30%. In summary it can thus be concluded that the isomerization of 1,2,4-TMB was the fastest primary reaction.

The reaction network in Fig. 5 does not show isomerization reactions within the xylene, TMB, and the TeMB fractions. Figure 6 shows that the isomer distributions in the xylene, TMB, and TeMB fractions depend on the extent of conversion. The thermodynamic equilibrium between the
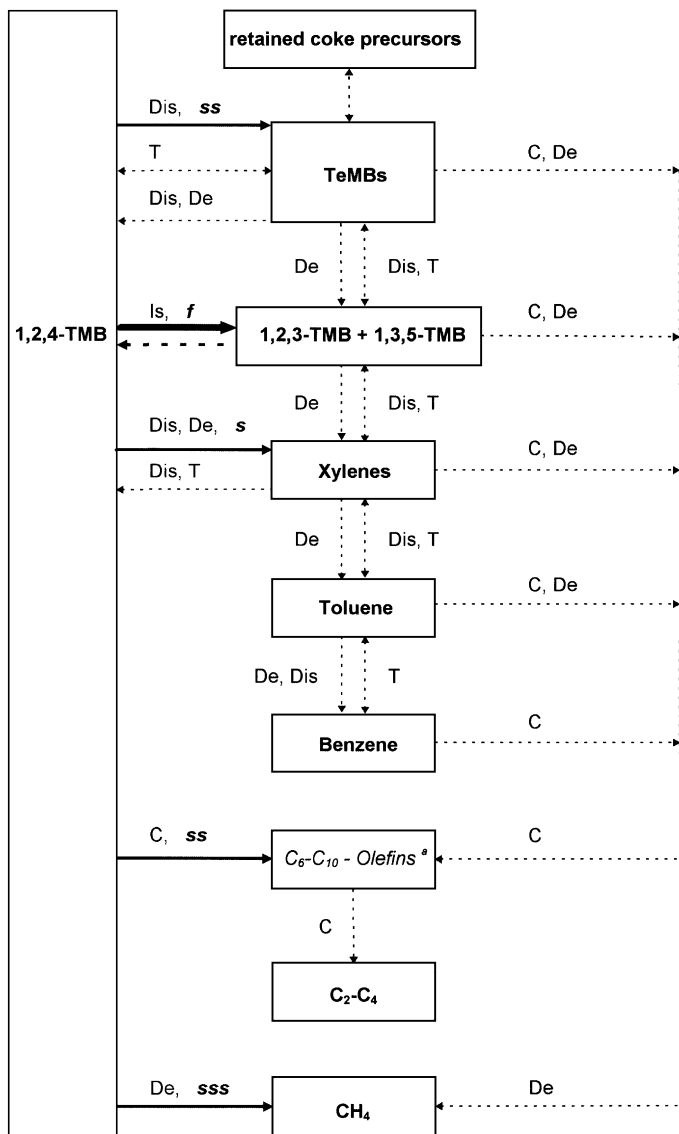
FIG. 5. Proposed reaction network of 1,2,4-TMB over HZSM-5. (i) Dis, disproportionation; Is, isomerization; De, dealkylation; C, cracking; (ii) f, fast; s, slow; ss, slower; sss, very slow; (iii) solid lines, primary reactions; dashed lines, secondary reactions. [a]Product not observed.

isomers of each fraction is reached at conversion levels of 20–35% which are obtained at space times between 4 and 20 min. Consecutive reactions other than isomerization reactions may disturb the equilibrium distribution due to selective consumption or formation of one of the isomers. However, if the isomerization is faster than the disturbing consecutive reaction, the equilibrium composition is maintained. Considering that isomerization is the fastest primary reaction of 1,2,4-TMB (Table 1), product isomerization may also play a role as fast consecutive reaction as illustrated in Fig. 7. A consecutive direct isomerization from 1,2,3-TMB to 1,3,5-TMB or the reverse is likely to be negligibly slow, since two methyl groups would have to shift simultaneously

or a methyl group has to migrate via several positions on the aromatic ring (vide introduction). The same can also be said for the direct isomerization between o-oxylene and p-xylene or between 1,2,4,5-TeMB and 1,2,3,4-TeMB.

At conversions lower than 25% 1,2,4,5-TeMB showed the highest mole fraction amongst the TeMB isomers (Fig. 6a). Depending on the disproportionation mechanism, the selective formation of 1,2,4,5-TeMB relative to 1,2,3,4-TeMB and 1,2,3,5-TeMB may be interpreted as a transition state shape selective effect or as a product shape selective effect (3). A generally accepted disproportionation mechanism of alkylaromatics involves a biphenylic transition state intermediate as proposed by Csicsery for the transalkylation of alkylbenzenes over mordenite catalysts (15, 16). Amongst the possible transition state intermediates (5, 17, 18) in the disproportionation of 1,2,4-TMB the most linear one is sterically favoured inside the micropores. The decomposition of this particular transition state yields 1,2,4,5-TeMB. However, at high temperatures and in the sterically restrictive environment of the micropore system, disproportionation may occur via a less space consuming dealkylation- or alkylation-type mechanism (19). If this mechanism is dominant, the micropore system selectively forms 1,2,4,5-TeMB due to its minimum van der Waals diameter being the lowest amongst the TeMB isomers (2). At higher conversions the equilibrium composition of the TeMB fraction is observed as represented by the solid lines in Fig. 6a. This is proposed to occur via consecutive isomerization of 1,2,4,5-TeMB on the external surface.

The consistent explanation of the selective formation of 1,2,4,5-TeMB in terms of shape selectivity strongly indicates that 1,2,4,5-TeMB can be formed within the micropore system of ZSM-5. The formation of 1,2,4,5-TeMB inside the micropores of ZSM-5 is consistent with observations made by Yashima *et al.* (20). In the methylation of 1,2,4-TMB over ZSM-5 they observed that 1,2,4,5-TeMB was formed with a high selectivity. They also concluded that 1,2,4,5-TeMB was mainly formed in the micropores, while 1,2,3,4-TeMB, 1,2,3,5-TeMB, 1,2,3-TMB, and 1,3,5-TMB were formed on the external surface. During the methanol to gasoline reaction, Anderson and Klinowski (21), by means of NMR studies, observed 1,2,3-TMB, 1,3,5-TMB, and all three TeMB isomers in the adsorbed phase, thus being accommodated inside the micropores of ZSM-5. They suggested that at high temperature ($T \geq 643$ K) these relatively large species, amongst them 1,2,4,5-TeMB, are able to leave the crystallite because of the increased effective channel diameter. The formation of these products on the external surface, however, was not considered.

The initial selective formation of p-xylene (Fig. 6c), which has the smallest kinetic diameter of the xylene isomers, indicates that the xylene distribution is affected by product shape selectivity. However, xylenes can be formed via several primary reactions (Fig. 5). Depending on the reaction
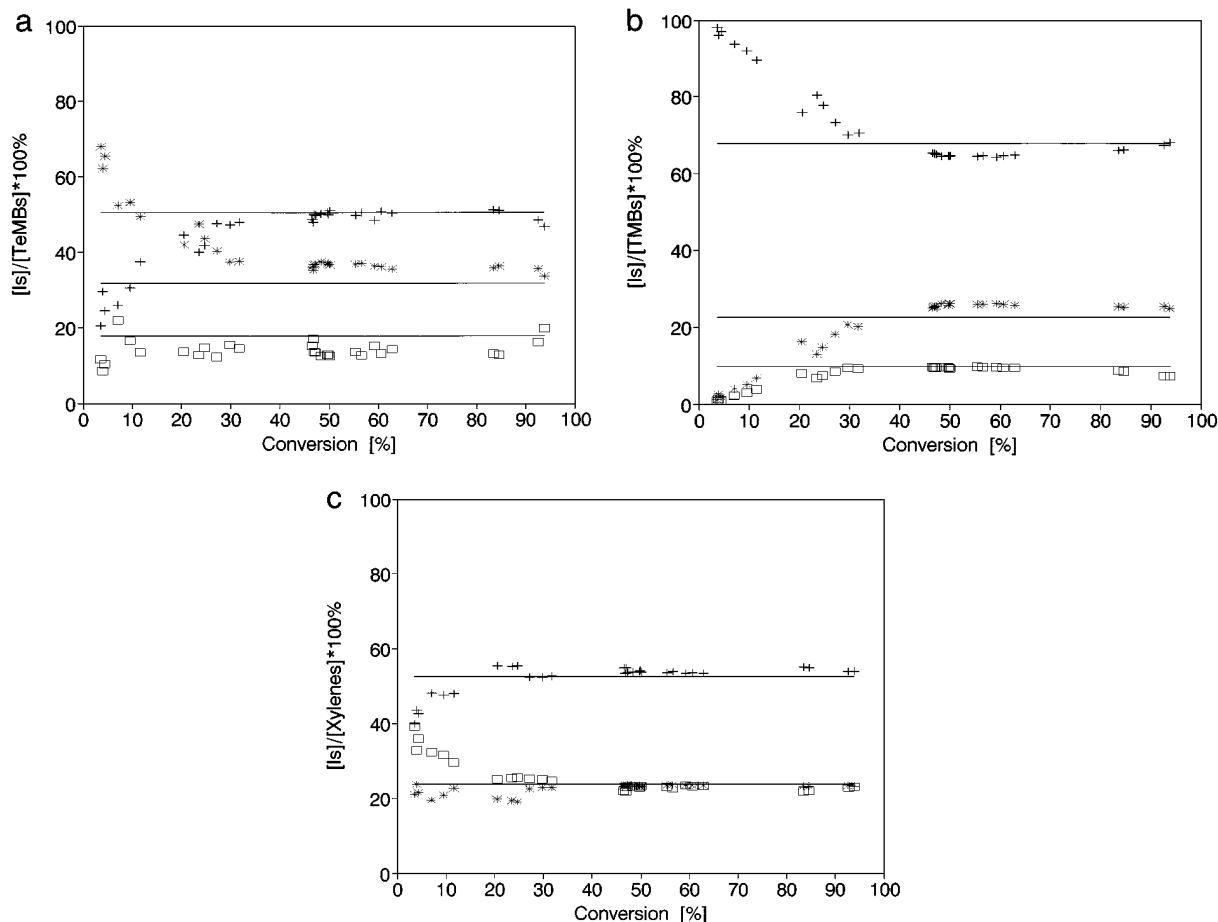
FIG. 6. Influence of conversion on the isomer distribution in the TeMB, TMB, and xylene fraction during the transformation of 1,2,4-TMB over HZSM-5 [$T = 723$ K; $p_{1,2,4\text{-TMB, in}} = 3.5$ kPa]. (a) □, 1,2,3,4-TeMB; +, 1,2,3,5-TeMB; *, 1,2,4,5-TeMB; (b) □, 1,2,3-TMB; +, 1,2,4-TMB; *, 1,3,5-TMB; (c) □ *p*-xylene; +, *m*-xylene; *, o-xylene. Equilibrium fractions of the respective isomer shown as solid lines.

and on the reaction mechanism, restricted transition state selectivity may also play a role. However, from the present reaction data set it is not possible to distinguish between product- and transition state selectivity. With increasing space time the distribution of xylenes reaches equilibrium, as shown by the solid lines in Fig. 6. This is due to consecutive isomerization reactions.

The reaction network shown in Fig. 5 is consistent with the findings of Ko and Kuo (5) for the conversion of 1,2,4-TMB over HY zeolite. However, since their reaction temperatures were between 473 and 573 K, compared to 723 K in the present work, negligible light cracking or dealkylation products were observed. In contrast to the observations in this work they proposed the disproportionation reaction to be faster than the isomerization reaction. This may be due to various factors, such as the different reaction temperatures and the zeolite type (pore size, Si/Al). They also proposed toluene to be a secondary stable product while benzene was not observed. Using zeolite Y, the formation of pentamethylbenzene was reported, which was not ob-

served in the present work. Due to the smaller pore-size of HZSM-5 relative of HY, the formation of tetra- and pentamethylbenzene will be more inhibited in the former case. Since the product concentration of TeMBs is already very small and the conversion of TeMBs to pentamethylbenzene is sterically highly inhibited over ZSM-5, no pentamethylbenzene was observed in the product stream. It may, however, be present as a coke precursor in the channel intersections of ZSM-5.

Due to consecutive reactions, the reaction network for the conversion of 1,2,4-TMB as illustrated in Fig. 5 is too complex to make it useful as a probe reaction. However, the secondary and reverse reactions can generally be minimised by converting 1,2,4-TMB at low space times, i.e., at low conversion levels, at which the reaction network may become as simple as the one illustrated in Fig. 7. Since primary disproportionation, dealkylation, and cracking of 1,2,4-TMB were relatively slow compared to the isomerization reaction, it is deduced that the consumption of TMB and TeMB isomers in the same type of secondary reactions is also slow
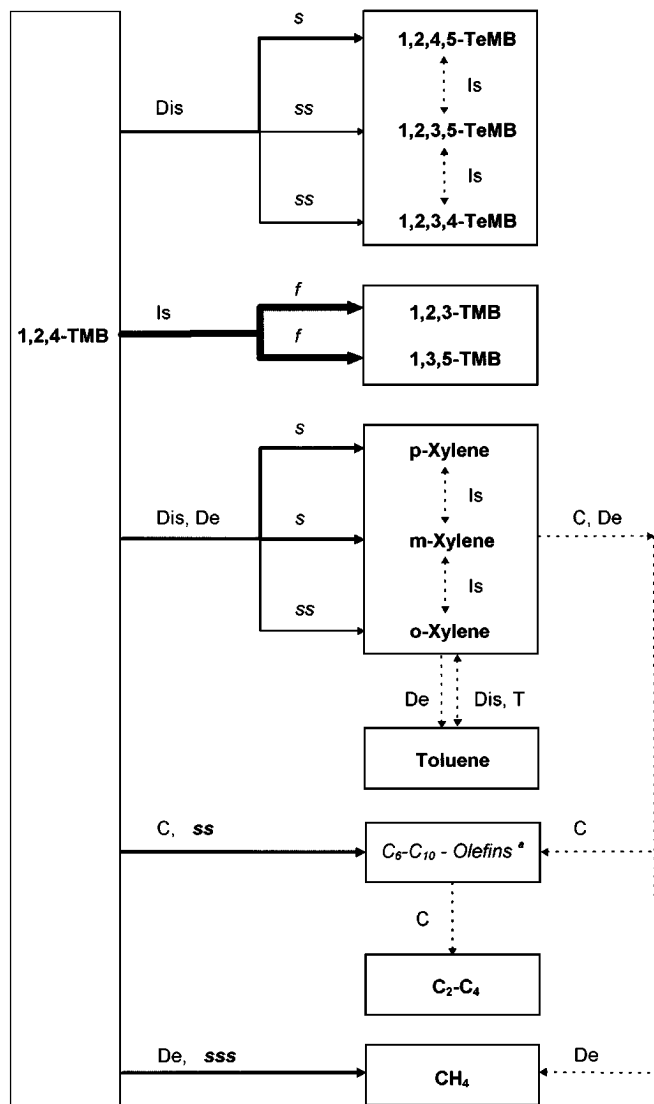
FIG. 7. Simplified reaction network of 1,2,4-TMB over HZSM-5 for low conversion levels. (See Fig. 5 for abbreviation key.)

and may therefore be neglected. However, these reactions may be relatively fast in the case of the xylenes, as indicated by the appearance of toluene as an apparent primary product.

CONCLUSION

A reaction network for the transformation of 1,2,4-TMB over HZSM-5 has been proposed. At low conversions (5–10%), secondary and reversible reactions are minimised and the reaction can be described by a relatively simple reaction network (Fig. 7). Under these conditions it is reasonable to assume that the rates of formation of 1,2,3-TMB and 1,3,5-TMB are equal to the rate of the respective isomerization reactions of 1,2,4-TMB and thus reflect the isomerization activity of the catalyst. Product distributions in the xylene and tetramethylbenzene fraction are not thermodynamically controlled and thus represent valuable information on the selectivity of HZSM-5. As expected the conversion affects the product distribution, confirming that selectivities of different ZSM-5 catalysts have to be compared at equal conversions.

REFERENCES

1. Weitkamp, J., and Ernst, S., *Catal. Today* **19**, 107 (1994).
2. Röger, H. P., Möller, K. P., and O'Connor, C. T., *Microporous Mater.* **8**, 151 (1997).
3. Csicsery, S. M., *ACS Monogr.* **171**, 680 (1976).
4. Gilson, J. P., and Derouane, E. G., *J. Catal.* **88**, 538 (1984).
5. Ko, A. N., and Kuo, C. T., *J. Chin. Chem. Soc.* **41**, 145 (1994).
6. Collins, D. J., Quirey, C. B., Fertig, J. E., and Davis, B. H., *Appl. Catal.* **28**, 35 (1986).
7. Chao, K., and Leu, L., *Zeolites* **9**, 193 (1989).
8. Gnep, N. S., Tejada, J., and Guisnet, M., *Bull. Soc. Chim. Fr.* **1–2**, 5 (1982).
9. Schulz, H., and Nehren, S., *Erdöl Kohle* **39**, 93 (1986).
10. Wakao, N., and Funazkri, T., *Chem. Eng. Sci.* **33**, 1375 (1978).
11. Chu, C. F., *et al.*, *AIChE J.* **35**, 146 (1989).
12. Moulijn, J. A., Tarfaoui, A., and Kapteijn, F., *Catal. Today* **11**, 1 (1991).
13. Gierman, H., *Appl. Catal.* **43**, 271 (1988).
14. Levenspiel, O., "Chemical Reaction Engineering," 2nd ed. (a) p. 109, (b) p. 185. Wiley, New York, 1972.
15. Csicsery, S. M., *J. Catal.* **19**, 394 (1970).
16. Csicsery, S. M., *J. Catal.* **23**, 124 (1971).
17. Cartraud, P., Cointot, A., Dufour, M., Guisnet, N. S., Joly, G., and Tejada, J., *Appl. Catal.* **21**, 85 (1986).
18. Kikuchi, E., Matsuda, T., Fujiki, H., and Morita, Y., *Appl. Catal.* **11**, 331 (1984).
19. Dooley, K. M., Brignac, S. D., and Price, G. L., *Ind. Eng. Chem. Res.* **29**, 789 (1990).
20. Yashima, T., Inaka, A., and Namba, S., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)* **28**(1), 13 (1985).
21. Anderson, M. W., and Klinowski, J., *Nature* **339**, 200 (1989).