

Standard reaction of the International Zeolite Association for acidity characterization: Ethylbenzene disproportionation over LaNaY[☆]

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Dedicated to Professor Dr. Ing. Jens Weitkamp on the occasion of his 60th birthday

Abstract

Results from five laboratories participating in the Catalysis Commission of the International Zeolite Association are presented for the disproportionation of ethylbenzene over a LaNaY catalyst. Despite the complexity of this reaction, with temperature-dependent induction phenomena and catalyst deactivation, the data from different sources are in fair agreement. Attention is drawn to a series of experimental parameters, e.g. reactor and saturator setup and chromatographic parameters, that are important for obtaining reproducible results.

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1. Introduction

The Catalysis Commission of the International Zeolite Association (IZA), together with, for in-

stance, the Structure and Synthesis Commissions, is one of the five working groups that intend to serve the zeolite community by providing uniform nomenclature and reliable synthesis and reaction procedures [1]. For industrial or academic groups that are not familiar with zeolite catalytic reactions, or even for established teams, it is desirable to compare the results obtained in their own, often home-built reactors, with data obtained in other groups. By publishing established procedures and

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results of test reactions, it is the intention of the Commission to provide readily accessible reference data. The present paper reports on the first of such reference reactions, namely the disproportionation of ethylbenzene over acid zeolites. In the past similar initiatives have been undertaken by consortia of European catalysis laboratories, for instance with the standard hydrogenation catalyst EuroPt-1, or the hydroxylation catalyst EuroTS-1 [2–4].

Apart from the detailed standard procedure for catalyst preparation and the catalytic reaction, we also give a format for data calculation and presentation. In the data presentation, the five laboratories involved have been labeled in a random way as L1, L2, L3, L4 and L5. We briefly indicate how our standardized results fit within previously reported literature data. Finally, the problems and pitfalls that can be encountered in obtaining reproducible results will be discussed.

2. Experimental procedures

2.1. Purification of the ethylbenzene feed

In order to remove impurities such as ethylbenzene hydroperoxide or 1-phenylethanol, the ethylbenzene was passed over a column with 1–1.5 cm internal diameter, filled with 25–35 ml alumina freshly activated by calcination at 723 K (Al_2O_3 for chromatography, Fluka 06300). The chromatographic column was kept in an inert atmosphere during this operation. Pure ethylbenzene should not give any color when 1 ml is mixed with about 0.2 ml of concentrated sulfuric acid.

2.2. Catalyst preparation

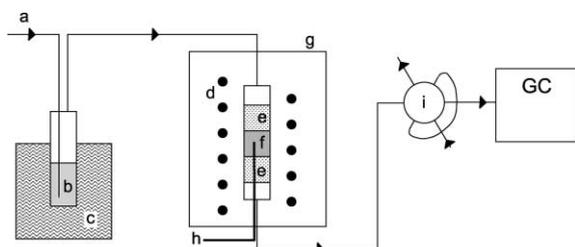
LaNaY zeolite was prepared in L2 as follows, starting from a NaY zeolite ($\text{Si}/\text{Al} = 2.4$) from Degussa AG. The zeolite is first saturated with water in a desiccator over saturated aqueous $\text{Ca}(\text{NO}_3)_2$. Thermogravimetric analysis (TGA) indicates that the water content of the moist sample is 24.2 wt.% with respect to the total weight of the moist zeolite sample. 166.5 g of the moist zeolite, corresponding to 126.2 g dry zeolite is suspended

in 400 ml water, to which 41.0 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 50 ml water is added. If needed, the pH is adjusted with dilute NaOH until it is above 5.5. After adjusting the volume to 500 ml, the stirred suspension is heated at 353 K for 18 h. The suspension is filtered while hot and washed with 1.5 l water. After re-suspension of the filter cake in 400 ml water, a second exchange is performed with an identical procedure, followed by a third and a fourth exchange. After the fourth exchange, the zeolite is washed until nitrate-free as checked with Lunge's reagent (Zn dust, sulfanilic acid, α -naphthylamine), air-dried, and dried for 24 h in an oven at 373 K. Samples were distributed among the participating laboratories. The degree of La exchange is $\approx 72\%$ of the total ion exchange capacity.

The catalyst was granulated by pressing without a binder, under a maximum pressure of 400 MPa, crushed and sieved to obtain particles with a diameter between 0.2 and 0.3 mm. In order to know the water content of these particles, a TGA experiment was performed on these granules. A catalyst weight corresponding to 0.29 g dry catalyst was then diluted with 3 ml washed sand or quartz chips (0.1–0.3 mm particle size). The dilution allows to have an appropriate catalyst bed height, particularly when working with small amounts of catalyst.

2.3. Apparatus and reaction procedure

The catalyst, diluted with the inert material, was introduced into a 1 cm internal diameter reactor made of glass or quartz (Scheme 1). The catalyst is held in place by inert structures such as glass frits or quartz wool plugs. The temperature is controlled with a thermocouple placed centrally in the catalyst bed. Flows are passed through the bed from top to bottom. The catalyst is pretreated inside the reactor by heating in a 50 ml per min N_2 flow, at a rate of 2 K per min up to 523 K. This temperature is maintained for 12 h. After that, the reactor is brought to the reaction temperature (453, 523 or 593 K). After 2 more h of equilibration at the reaction temperature, the reaction is initiated. The N_2 carrier flow (40 ml per min) is first saturated with ethylbenzene by passing through a well thermostated saturator at 294 K.



Scheme 1. Reactor setup for ethylbenzene disproportionation: (a) N₂ gas flow, (b) saturator with ethylbenzene, (c) thermostated bath, (d) heating coils for glass reactor, (e) inert structures, (f) bed of diluted catalyst, (g) oven, (h) thermocouple, (i) 6-way valve. Transfer lines between reactor and GC should be heated. Proper air circulation in the oven should be provided.

Given the vapor pressure of ethylbenzene, this corresponds to a flow of 1.0 mmol h⁻¹.

Analysis is preferentially performed by on-line sampling and gas chromatographic separation, e.g. on a CP-Sil5 column or a Carbowax column. The sequence of products is in both cases benzene (Bz), ethylbenzene (E-Bz), *meta*-, *para*- and *ortho*-diethylbenzene (DE-Bz), possibly followed by triethylbenzenes. At the rather low conversion levels studied, the summed triethylbenzenes amounted to <0.5% of the total aromatics. A typical temperature program for a CP-Sil5 column is: 5 min at 403 K, followed by heating at 5 K min⁻¹ to 523 K; final time at 523 K for 10 min. On a Carbowax column, the products can be isothermally separated at 343 K.

The integrated area for each compound $i(A_i)$ was converted to a corrected area (a_i) by multiplying with an FID response factor (f_i) and dividing by the molecular weight M_i

$$a_i = A_i f_i / M_i$$

The corrected areas a_i are mole-proportional figures. Typical FID response factors are $f_{\text{Bz}} = 1.000$, $f_{\text{E-Bz}} = 1.019$, $f_{\text{DE-Bz}} = 1.031$; however, L1 and L3 determined the sensitivity factors characteristic for their chromatograph and sampling setup. Conversion (X) and yields (Y) are calculated as follows:

$$X_{\text{E-Bz}} = (a_{\text{Bz}} + a_{\text{DE-Bz}}) / (a_{\text{Bz}} + a_{\text{E-Bz}} + a_{\text{DE-Bz}})$$

$$Y_{\text{Bz}} = 2a_{\text{Bz}} / (a_{\text{Bz}} + a_{\text{E-Bz}} + a_{\text{DE-Bz}})$$

$$Y_{\text{DE-Bz}} = 2a_{\text{DE-Bz}} / (a_{\text{Bz}} + a_{\text{E-Bz}} + a_{\text{DE-Bz}})$$

The experiments were at least performed twice in each laboratory, and generally the agreement between such runs was very good, i.e. <5% variation. Only one representative experiment is given for each group.

3. Results

Ethylbenzene conversions are plotted as a function of time on stream for reactions at 453, 523 and 593 K in Figs. 1–3 respectively. Generally, the conversion increases during an induction period; it then stays stable, or, particularly at the higher temperatures, it slowly decreases due to catalyst deactivation. At first sight, the scatter in the data seems rather large, but this is usually due to a deviation of a single lab: thus L4 obtains low conversions at 453 K, while L5 observes unusually high conversions at the higher reaction temperatures. There are also differences in the time dependence of the conversion. Thus, in the experiments at 453 K (Fig. 1), the induction period is short in L2, and much longer in L1; L3 and L5

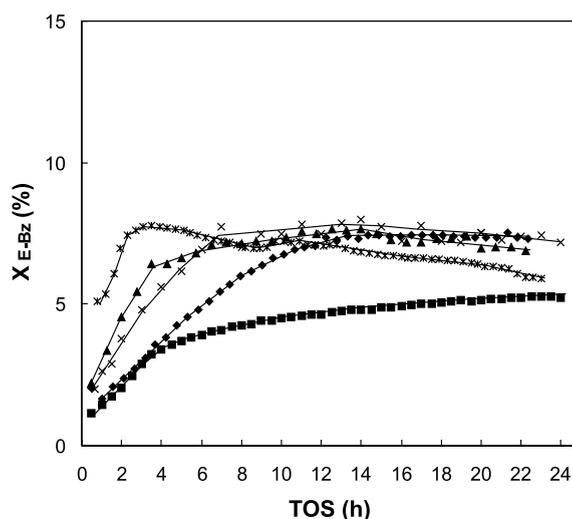


Fig. 1. Conversion of ethylbenzene ($X_{\text{E-Bz}}$) as a function of time on stream. Data from L1 (◆), L2 (×), L3 (▲), L4 (■) and L5 (×). Conditions: 290 mg dry LaNaY catalyst, N₂ carrier flow, $W/F_{\text{E-Bz}} = 290 \text{ g h mol}^{-1}$, 453 K.

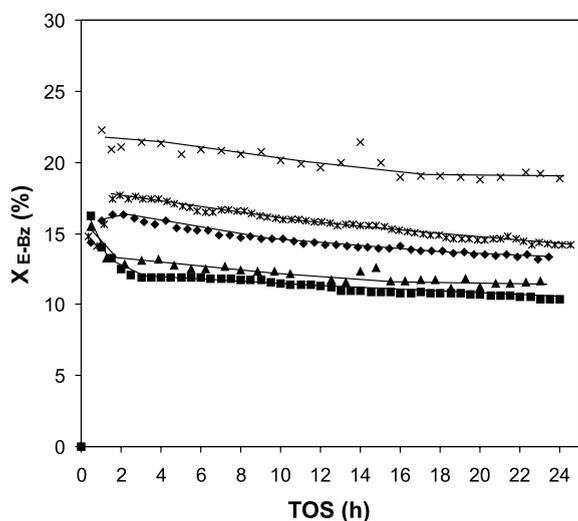


Fig. 2. Conversion of ethylbenzene (X_{E-Bz}) as a function of time on stream. Data from L1 (\blacklozenge), L2 (\blacktimes), L3 (\blacktriangle), L4 (\blacksquare) and L5 (\times). Conditions: as in Fig. 1, but reaction temperature = 523 K.

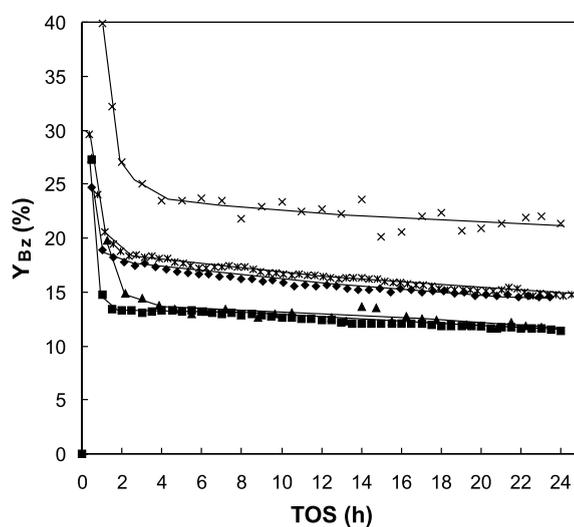


Fig. 4. Yield of benzene (Y_{Bz}) as a function of time on stream. Data from L1 (\blacklozenge), L2 (\blacktimes), L3 (\blacktriangle), L4 (\blacksquare) and L5 (\times). Conditions: as in Fig. 1, but reaction temperature = 523 K.

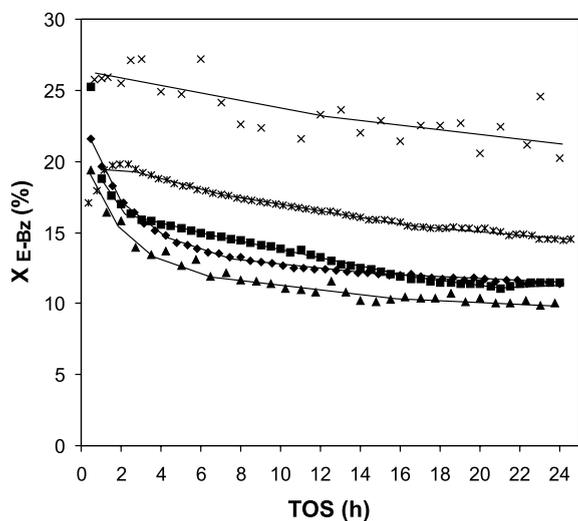


Fig. 3. Conversion of ethylbenzene (X_{E-Bz}) as a function of time on stream. Data from L1 (\blacklozenge), L2 (\blacktimes), L3 (\blacktriangle), L4 (\blacksquare) and L5 (\times). Conditions: as in Fig. 1, but reaction temperature = 593 K.

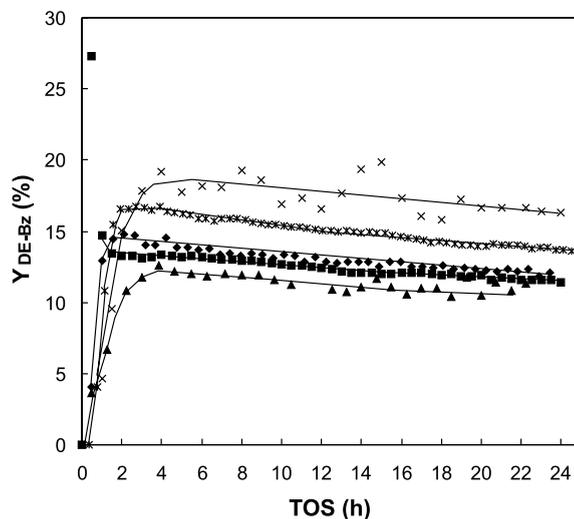


Fig. 5. Yield of diethylbenzenes (Y_{DE-Bz}) as a function of time on stream. Data from L1 (\blacklozenge), L2 (\blacktimes), L3 (\blacktriangle), L4 (\blacksquare) and L5 (\times). Conditions: as in Fig. 1, but reaction temperature = 523 K.

obtain practically the same result. At 523 and 593 K, there is hardly an induction period.

Yields of benzene and diethylbenzenes as a function of time are given in Figs. 4 and 5 respectively, for the reactions at 523 K. Initial benzene yields are high, while the diethylbenzene

yields gradually increase during the induction period. The differences among the laboratories parallel the deviations observed in Fig. 2 for the conversion of ethylbenzene.

The ratio of diethylbenzene yield over benzene yield gives an idea of the amount of ethyl groups

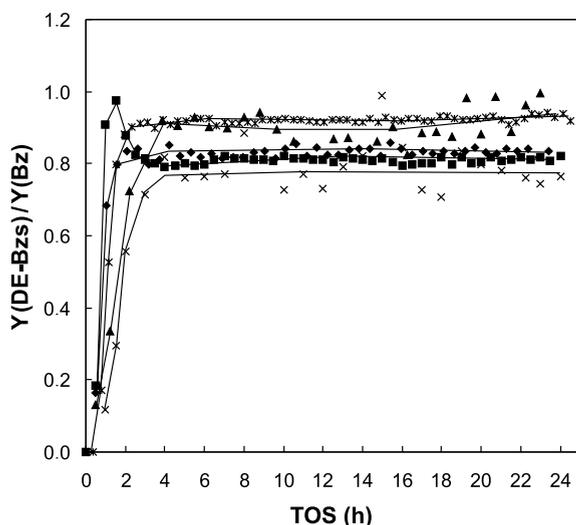


Fig. 6. Ratio of diethylbenzene yield over benzene yield for the reaction at 523 K. Data from L1 (◆), L2 (✱), L3 (▲), L4 (■) and L5 (×). Conditions: as in Fig. 1, but reaction temperature = 523 K.

that are lost from the aromatic molecules in the disproportionation reaction, and of the amount of ethylbenzene that is transformed into polyalkylated molecules that stay adsorbed in the zeolite. Since in the initial phase much more benzene than diethylbenzene is formed, the yield ratio increases during the induction period to eventually reach a constant value. An example is shown in Fig. 6, for the reactions at 523 K. There is good agreement, even if the yield ratio strongly fluctuates in L5. The ratio of diethylbenzene over benzene yield markedly decreases with increasing reaction temperature, with average values of 0.92, 0.85 and 0.67 for 453, 523 and 593 K respectively (see Table 1).

The best agreement between the different laboratories is found for the isomer distribution. Early in the induction period, *para*-diethylbenzene may be the dominant isomer, but the selectivity quickly decreases at the expense of *meta* and *ortho* (Fig. 7). After the induction period, *meta* is always the dominant isomer, followed by *para* and *ortho*. With increasing temperature, the *meta* and *para* fractions slightly decrease, while the *ortho* fraction increases. After the induction period, the same distribution is obtained in all laboratories with a typical standard deviation of 1%. The only ex-

Table 1

Statistical evaluation of reaction parameters after 20 h time on stream at 453, 523 and 593 K

	453 K	523 K	593 K
X_{E-Bz} (%)	6.7 ± 1.0	13.7 ± 3.2	13.9 ± 4.2
Y_{Bz} (%)	7.0 ± 1.3	20.9 ± 3.6	16.8 ± 5.9
Y_{DE-Bz} (%)	6.4 ± 0.7	16.6 ± 2.8	11.0 ± 2.9
Y_{DE-Bz}/Y_{Bz}	0.92 ± 0.11	0.85 ± 0.06	0.67 ± 0.13
$S_{1,3-DE-Bz}$ (%)	64.1 ± 3.4	63.4 ± 1.0	62.4 ± 1.2
$S_{1,4-DE-Bz}$ (%)	32.8 ± 1.9	30.5 ± 0.9	30.3 ± 0.9
$S_{1,2-DE-Bz}$ (%)	3.1 ± 1.8	6.2 ± 0.8	7.3 ± 1.3

Averages and standard deviations were calculated for the population of five participating laboratories.

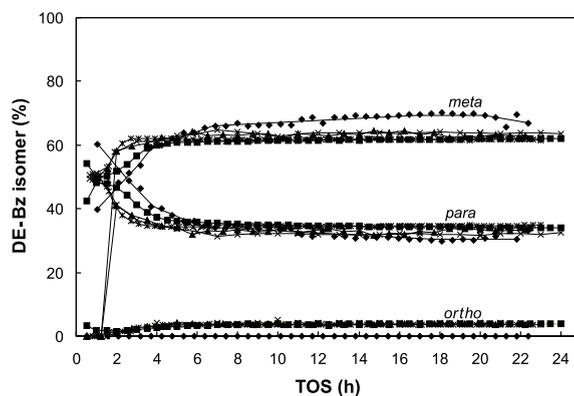


Fig. 7. Selectivities to the diethylbenzene isomers (%) in the ethylbenzene disproportionation as a function of time on stream. Reaction temperature = 453 K.

ception is the *ortho* content for the reaction at 453 K in L1. Clearly, at low conversion, the minor *ortho* isomer was not detected with the GC settings used.

4. Discussion

The ethylbenzene disproportionation has been studied in detail as a test to characterize the pore size and the number of acid sites in zeolites [5–14]. Particularly clear insights have resulted from the work of the Weitkamp and Karge groups [6–11]. In the generally accepted view, the induction period observed for 12-membered ring zeolites corresponds to the formation of higher alkylated aromatics, such as polyalkylated diphenylethanes,

in the interior void volume of the zeolites [5,6]. In the present data (Fig. 1), the induction period generally lasts between 7 and 11 h for a reaction at 453 K. Since the polyalkylated diphenylethanes contain more than one ethyl group per aromatic nucleus, the product molecules in the induction period contain on the average less than one ethyl group per aromatic group; as a result, the benzene yield is initially higher than the yield of diethylbenzenes, as shown for example in Figs. 4 and 5 for the reaction at 523 K. In the stationary regime at 453 K, the benzene and diethylbenzene yields are approximately equal, corresponding to a stoichiometric ethylbenzene disproportionation (see Table 1). At the higher reaction temperatures, the conversion decreases almost immediately after the start of the experiment, which means that the induction period is much shorter. Moreover, the $Y_{\text{DE-Bz}}/Y_{\text{Bz}}$ ratios are lower than one, since part of the ethylbenzene is cracked [7]. For reactions at 523 and 593 K, the conversion slowly decreases as a function of time due to catalyst deactivation. Such a deactivation was not perceived by most of the laboratories for the reaction at 453 K.

The isomer distribution, even at steady state, often clearly deviates from the thermodynamic equilibrium. Literature data show that for reactions at 453–473 K, the stationary *para* selectivity increases in the order H-L < H-Beta \sim LaNaY < LaNaEMT < H-MCM-22 [8]. The data of the five laboratories are in excellent agreement with previously reported data on LaNaY catalysts. Initially, the *para* product prevails. In an electrophilic substitution, both *ortho* and *para* positions are electronically activated. However, the *para* position is favored because of steric hindrance of the ethyl group. The *meta* isomer is thermodynamically more stable and is obtained by secondary isomerization. As the activity of the catalyst increases during the induction period, secondary isomerization leads to more *meta* isomer via a transalkylation mechanism [6]. In 10-MR zeolites such as H-ZSM-5, the transalkylating diarylethanes cannot be formed because there is insufficient space inside the pores. Therefore, some authors have proposed that the reaction proceeds via dealkylation and realkylation rather than through transalkylation [7]. A reaction in a 10-MR

zeolite requires higher temperature and it does not display an induction period. Moreover, in H-ZSM-5, the *para* isomer prevails, since it is favored not only by the kinetics but also by the shape selectivity [11,13,14]. Additionally, the catalyst displays little isomerization activity.

While all observations are qualitatively the same for the participating laboratories, the quantitative agreement could have been better. An overview of the reaction parameters after 20 h on stream is given in Table 1, together with the standard deviations. During the work, several critical factors were identified that may lead to aberrant results:

1. First, instead of using the granulated catalyst as such, it was diluted with quartz. This way, a too fast catalyst deactivation due to backmixing of reaction products can be avoided.
2. Another important precaution is the use of highly purified ethylbenzene. Too fast deactivation may be due to the oxygenated aromatics in the impure feed. Concerning this and the former point, it can be observed that for all reaction temperatures, deactivation occurs to a similar degree in all laboratories.
3. The saturator is obviously crucial: the residence time of the gas flow must be sufficiently long to ensure near to complete saturation of the flow. Design of saturators has been discussed in detail in the literature [15,16]. While the temperature of the bath surrounding the liquid reservoir may be constant and easily controlled, the temperature of the liquid itself may be slightly different because of the constant influx of N₂; hence it may not always be easy to determine the precise temperature inside the saturator.
4. Accurate reaction temperature control, within one degree, seems critical. High initial conversions may be due to a temperature overshoot. Reaction temperatures can only accurately be measured if the thermocouple is introduced inside the catalyst bed. Ventilation of the oven may help to achieve a homogeneous temperature profile around the reactor tube. Note that for a hypothetical apparent activation energy of 80 kJ mol⁻¹, a temperature difference of two degrees may result in a rate increase with 10%!

5. Similarly, it was found useful to insert a delay time of 2 h between the cooling of the reactor from the pretreatment to the reaction temperature and the actual reaction start. This allows a complete thermal equilibration of the reactor oven.
6. Quantitative determination of product distributions is largely related to a correct gas chromatographic procedure. For different diethylbenzene isomers, agreement is obviously excellent, since the same response factors can be used. However, the diethylbenzene over benzene ratios are less accurate, partly because response factors may easily vary with a few percent for different FID detectors.
7. Splitless injection of the gas sample into the GC is the least susceptible to errors. This implies that a very small loop volume should be collected with the sampling valve. If a splitter is used, the variable volatility of the compounds may result in different gas compositions in the injected flow and the waste flow. Even a slightly varying split flow can then induce serious errors.

In order to improve the reliability of the GC analyses, one laboratory (L5) has tried the use of an internal GC standard, viz. n-decane. Such a standard should only be added to the reaction mixture after pass through the reactor, since adsorption of the standard on the catalyst may interfere with the complex sorption and desorption phenomena, e.g. during the induction period [10]. The use of the internal standard indicated that at the start of the reaction, there is indeed some deficiency in the mass balance. The same observation is also easily made without an internal standard, since the total area of all peaks is somewhat smaller (e.g. ~10%) in the induction time than in the steady state. In the steady state, mass balances based on the internal standard proved to be quite satisfactory, within 5%. Therefore it was decided not to use an internal standard on a routine basis.

8. In the same context, it is essential to work in the linear range of the FID detector. This means that peaks should be considerably smaller than the maximum output signal. Meanwhile, integration parameters must be chosen so as to de-

tect even small peaks, for instance those of the *ortho* isomer at low conversions.

Considering the potential errors in saturation of the flow (3), in the control of reaction temperature (4) and determination of the GC response factors (6), it would be naive to expect less than 20% deviation on for instance stationary conversion.

5. Conclusion

In hindsight, the disproportionation of ethylbenzene on a 12-MR zeolite certainly is not the simple reaction that may allow to obtain similar results in different reactor setups. The reaction is complex due to the importance of sorption of reactants and products [10], due to the initial non-steady-state behavior with formation of active species in the micropores, and due to the deactivation. Moreover, the reaction mechanism clearly varies with time on stream. All these phenomena are strongly dependent on temperature and partial pressure, and thus are much influenced by a precise control of the reaction. Nevertheless, we demonstrate that reproducible results can be obtained in a ring test with five laboratories, if proper care is taken of a series of critical experimental parameters. Current and future efforts of the IZA Catalysis Commission will be directed towards simpler gas phase reactions with bifunctional catalysts, and towards liquid phase reactions with zeolite catalysts. Moreover, other reactor types than the simple fixed bed setup will be used.

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