The synthesis of cresol from toluene and N_2O on H[Al]ZSM-5: minimizing the product diffusion limitation by the use of small crystals

B. Vogel, C. Schneider, and E. Klemm*

Institute of Technical Chemistry I, University of Erlangen—Nuremberg, Egerlandstrasse 3, D-91058 Erlangen, Germany

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The direct hydroxylation of toluene with nitrous oxide to cresol has been studied on two different H[Al]ZSM-5 zeolites with an Si/Al ratio of around 25 and different crystal sizes (30–70 nm and 1–3 μm). The samples were activated by calcination and characterized by X-ray diffraction, temperature programmed desorption of ammonia, adsorption of nitrogen and transmission electron microscopy. For the two different crystal sizes, different macroscopic cresol yields and time on stream behaviours are observed. The sample having larger crystals shows a decrease in toluene conversion with increasing reaction temperature. For the smaller crystals an increase in toluene conversion, selectivity to cresol and amount of para-cresol in the cresol fraction with increasing reaction temperature is observed. The para-cresol selectivity is lower on the sample with the longer diffusion path. The findings are explained by product diffusion limitation caused by high reactivity and strong adsorption of the polar product cresol on H[Al]ZSM-5, resulting in a rapid deactivation of the larger crystals.

KEY WORDS: H[Al]ZSM-5; N_2O; cresol; crystal size; diffusion limitation.

1. Introduction

In the past decade, H[Fe]ZSM-5 and H[Al]ZSM-5 have attracted increased attention among several research groups as catalysts for the selective oxidation of benzene to phenol by N_2O [1–7]. Although the partial oxidation of substituted aromatics to the corresponding phenols by N_2O would lead to products of higher value, only a limited amount of data in the literature is available [4,5,8]. Cresol represents an intermediate of great interest. Via the direct hydroxylation of toluene with N_2O on H[Al]ZSM-5, a shape-selective partial oxidation could be realized by the restricted pore structure of MFI. In the case of acid catalysis, the shape selectivity of H[Al]ZSM-5 has been applied for numerous reactions [9].

The formation of functional organic compounds like cresol on zeolites, however, leads to a well-known paradox of heterogeneous catalysis [10,11]. Caused by the high polarity of the product cresol compared with the relatively unpolar reactant toluene, a product inhibition and a subsequent deactivation of the zeolite in this reaction seems to play an important role. Concerning consecutive reactions inside the narrow zeolite pores, the aromatic ring is even more activated by the additional hydroxyl group [12,13]. Indeed, for the direct hydroxylation of benzene to phenol the strong deactivation of the zeolite catalyst by the formation of coke was identified as a major problem for industrial applications [5,14].

For several non-oxidative reactions on H[Al]ZSM-5, the product yield and long-term stability of the catalyst could be enhanced using zeolites with small crystals [15–18]. We suggest that the length of the diffusion path, closely related to the crystal size of H[Al]ZSM-5, plays a key role in the shape-selective partial oxidation of toluene by N_2O. To our knowledge, reliable data and extensive investigations concerning the relevant catalyst properties for high yields of cresol and low deactivation rates in the case of the direct hydroxylation of toluene have not yet been published.

The aim of the present paper is to elucidate the influence of the crystal size of commercial H[Al]ZSM-5 samples in the direct hydroxylation of toluene by N_2O to cresol. This has been investigated by using a sample with nano-crystals (30–70 nm) having a large outer surface area and a short intracrystalline diffusion path. These zeolites are normally applied for reactions where high selectivities for an intermediate product are needed, such as the production of olefins from methanol [15–17]. As reference a sample with larger crystals (1–3 μm) has been tested. Providing a smaller external surface and a relatively long intracrystalline diffusion path, these zeolites are applied in acid-catalysed hydrocarbon reactions like the disproportionation of toluene using the product shape selectivity of the zeolite catalyst [19].

2. Experimental

The two H[Al]ZSM-5 samples were obtained from PQ Corporation and ALSI-PENTA Zeolithe GmbH. Physicochemical properties of the catalysts are given in table 1. The molar Si/Al ratio and the iron content caused by impurities were determined by ICP AES. Prior to the catalytic runs the samples were pelletized

* To whom correspondence should be addressed.

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Table 1
Chemical analysis of the zeolites

Commercial name	Supplier	Sample name	Modification	Si/Al	Fe content (wt%)
CBV 5020	PQ Corporation	A	parent	25	0.044
SM 55	ALSI-PENTA	B	parent	24	0,041
CBV 5020	PQ Corporation	A′	2 h at 900 °C	25	0.044
SM 55	ALSI-PENTA	B′	2 h at 900 °C	24	0.041

(1.0 mm to 1.4 mm) and activated by *ex situ* high temperature calcination at 900 °C as presented elsewhere [20]. Powder X-ray diffraction data were collected in the 2θ range of 5° to 500° at a scan rate of $0.002^\circ\,min^{-1}$ using a Phillips X'Pert pro with monochromatic Cu K_α radiation. The degree of crystallinity was evaluated according to the method described in [21] by the summation of the intensities of the typical diffraction peaks between $2\theta = 22^\circ$ and $2\theta = 25^\circ$.

Temperature programmed desorption (TPD) of ammonia was performed on an AMI-100 instrument (Altamira Instruments). The procedure is given elsewhere [22]. The quantification of the desorbed amount of ammonia was done by applying a pulse-calibration method.

Sorption measurements for the uncalcined and calcined zeolites were carried out by means of physisorption of nitrogen at 77 K using an ASAP-2000 (Micromeritics) instrument. The samples were pretreated for 2 h at 573 K under vacuum. The micropore volume of the zeolites was calculated using the *t*-plot method [23].

The coke content of the calcined samples after 134 min on stream for the hydroxylation of toluene with nitrous oxide was determined by using thermogravimetric analysis (TA Instruments SDT 2960).

The gas-phase hydroxylation of toluene with N_2O and the disproportionation of toluene were conducted in a stainless steel isothermal fixed-bed reactor (17.4 mm i.d., 300 mm length) operated at atmospheric pressure. The reactor was loaded with 2 g (dry mass) of catalyst. Prior to the catalytic runs, the zeolite was heated up in N_2 to 500 °C and kept for 2 h at this temperature under a nitrogen flow of $320\,N\,ml\,min^{-1}$. After the adjustment of the reaction temperature, the catalyst was exposed to the reactants. Toluene was introduced at a partial pressure of 40 mbar *via* a glass evaporator using N_2 as carrier gas. For both reactions, the weight hourly space velocity (WHSV) was $2.5\,h^{-1}$ and the modified residence time was chosen to be $90\,g\,min\,mol^{-1}$. In the case of the hydroxylation of toluene, the molar ratio N_2O/toluene was applied to 1:1 or 3:1. Toluene was obtained from Merck (LiChrosolv® >99.9%). Nitrous oxide was used in medical grade and supplied by Linde AG. Reaction temperatures were 400, 450, and 500 °C. The disproportionation of toluene was carried out at 500 °C with a toluene partial pressure of 40 mbar. All products were analysed by online GC analysis.

3. Results and discussion

3.1. Characterization

The X-ray diffraction (XRD) spectra (not shown) of the studied samples showed the characteristic pattern of the MFI structure. Due to the calcination step no significant changes in the spectra were observed. For both samples, the calcination resulted in a loss of crystallinity. Although it is known from the literature that high temperature calcination leads to a significant dealumination and dehydroxylation of H[Al]ZSM-5 [9], a relatively high thermal stability of the investigated ZSM-5 zeolites was found. The crystal size of the zeolites was studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The pictures for the two different uncalcined samples A and B are shown in figure 1. The pictures clearly show that sample A consists of crystals with a size between 30 and 70 nm whereas sample B has larger crystals with 1 to 3 μm diameter. No differences in size and shape were observed for the high temperature calcined samples. An average crystal size for each sample was determined and is given in table 2.

The values of the micropore volume, V_M, presented in table 2 were calculated by using the *t*-plot method [23]. For the uncalcined zeolites, a higher value for sample A was obtained. After high temperature treatment, a decrease of V_M for both zeolites was observed. This is in good agreement with the results of Hong and Fripiat [24] who found that for H[Al]ZSM-5 with increasing calcination temperature an increasing dealumination and a decrease of the micropore volume occurred.

The TPD of ammonia showed that the total amount of chemisorbed ammonia is significantly reduced for both samples during the calcination procedure. This is due to dehydroxylation and dealumination of the zeolite [9]. After deconvolution of the TPD spectra, the concentration of Brønsted acid sites was quantified [25]. As expressed by the concentration of Brønsted acid sites given in table 2, both hydroxylation catalysts (A′ and B′) exhibit a low level of Brønsted acidity. Only a slight difference in terms of the concentration of Brønsted acid sites was found.

There is ongoing discussion in the literature concerning the nature of the active sites for the hydroxylation of hydrocarbons with N_2O on ZSM-5-type zeolites [1–7]. However, it was found that the iron content has an

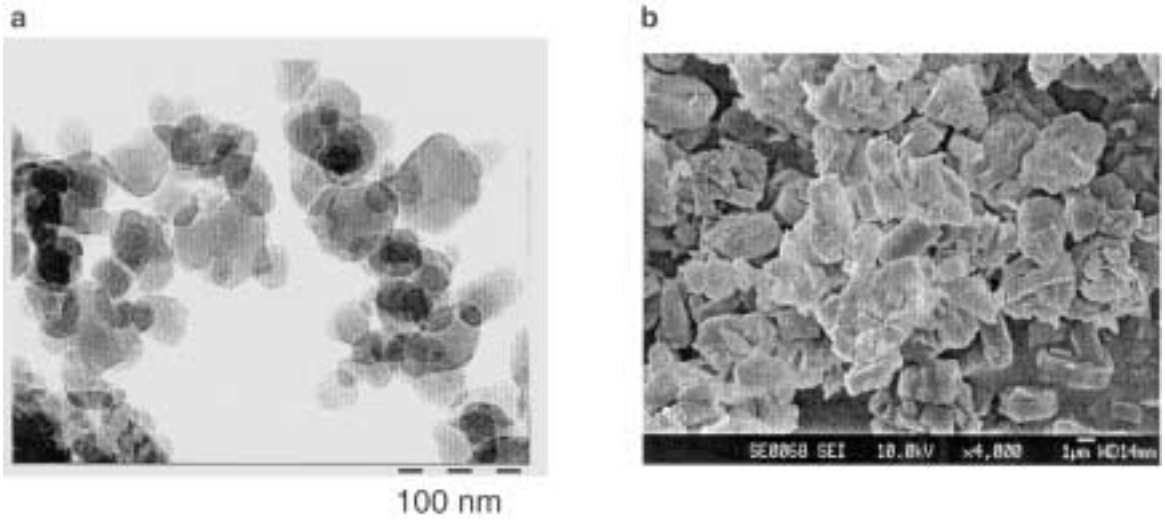

Figure 1. Electron micrographs: (a) sample A and (b) sample B.

influence on the activity of the zeolite catalyst [1,7]. We therefore determined the amount of iron impurities for the two samples (see table 1). No difference was found, within the experimental error. For the investigations discussed in the present article we can hence conclude that the difference in activity of the two samples is independent of the iron concentration.

3.2. Toluene disproportionation

To further characterize the acidity and the shape selectivity of the zeolites by a suitable test reaction, the disproportionation of toluene was carried out [26]. The toluene conversion and the selectivity to para-xylene at 500 °C on the calcined zeolites *versus* time on stream are shown in figure 2. The toluene conversion was found to be 2.5% for sample A′ and 3.5% for sample B′.

On sample A′, having smaller crystals and showing a lower conversion of toluene compared with sample B′, the para-xylene selectivity was found to be 30%. This is relatively close to the thermodynamic value at 500 °C and ambient pressure. For sample B′, which was supposed to show the performance of a high para-selective H[Al]ZSM-5 zeolite, a significant high para-xylene amount of 68% could be confirmed. Both zeolites show the expected performance concerning their shape-selective properties in the disproportionation reaction of toluene.

3.3. Toluene hydroxylation

Figure 3 shows the conversion of toluene versus the reaction temperature for the hydroxylation of toluene with N_2O on the two different zeolites. All conversions were determined after 15 min on stream. Para-, meta- and ortho-cresol, as well as benzene, xylenes and methyl-diphenylmethanes, were found in the product. No CO_2 was formed during our experiments.

Using a molar ratio of 1:1 the conversion of toluene increased with increasing reaction temperature for sample A′, whereas for the second zeolite (sample B′) a slight decrease with increasing temperature was found. At all reaction temperatures the toluene conversion on sample A′ was found to be higher than on sample B′.

Both zeolites exhibit a higher toluene conversion at 400 °C in the case of an excess of N_2O. Increased reaction temperatures reveal the same trends as for a molar ratio of 1:1. Sample B′, however, shows an even more significant decrease of the toluene conversion with increasing reaction temperature. Using a molar ratio of 3:1 at 500 °C on sample A′, no increase in the amount of converted toluene, compared with a reaction temperature

Table 2
Characterisation data of the catalysts

Sample name	Average crystal size (nm)	Relative crystallinity (%)	Micropore volume V_M ($N\,cm^3\,g^{-1}$)	Ac_{th} [a] (mmol H^+/g)	Ac_B [b] (mmol H^+/g)
A	50	78	0.129	0.640	0.57
B	2000	100	0.101	0.666	0.57
A′	50	66	0.119	0.640	0.32
B′	2000	92	0.081	0.666	0.35

[a] Calculated concentration of acid sites.
[b] Concentration of Brønsted acid sites determined from ammonia desorption at $T > 250$ °C.

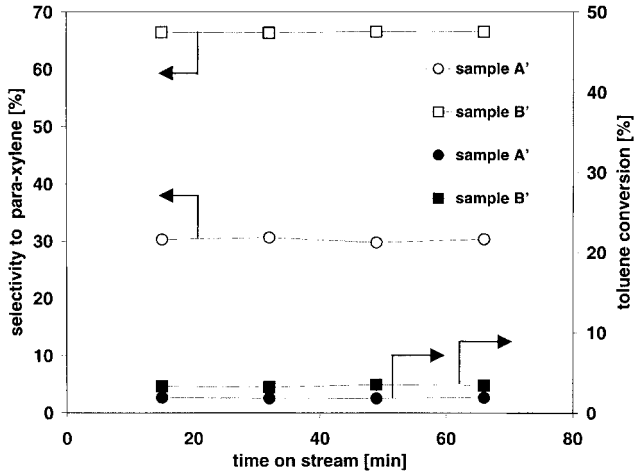

Figure 2. Selectivity to para-xylene and conversion of toluene *versus* time on stream for the disproportionation of toluene at 500 °C.

of 450 °C, is found. These observations indicate a strong dependence on the molar feed ratio and the reaction temperature for both zeolites in the hydroxylation of toluene with N_2O. From our point of view, the catalytic performance of sample B′ can only be explained by an increasing deactivation of the zeolite with increasing temperature. Assuming an Arrhenius function for the temperature dependency of the reaction rate, the initial activity on both samples is supposed to increase with increasing reaction temperature, hence resulting in a higher initial productivity of cresol. This leads to a high concentration of cresol inside the pores, favouring the adsorption of the products. The low volatility and the strong adsorption of the polar cresols implies a relatively long retention of the formed product inside the zeolite pores [27].

To avoid this phenomenon the desorption and the diffusion of the cresols from the catalyst surface could be enhanced by choosing a higher reaction temperature. This is confirmed in figure 4, where the selectivity to cresol versus the temperature is shown. For a stoichiometric feed ratio, the selectivity to cresol was observed to increase with increasing reaction temperature and increasing toluene conversion. A rise in selectivity combined with an enhanced toluene conversion is rather untypical and indicates a strong adsorption of primary formed cresol at low temperatures. Simultaneous consecutive reactions of the primary formed cresols will be enhanced by raising the reaction temperature. Thus, due both to the catalytic sites active for oxidation and to the acidity of the zeolites, the cresols can be further oxidized by N_2O or react in acid-catalysed reactions.

Further oxidation of para-, meta- and ortho-cresol leads to dihydroxy-, trihydroxy- or higher hydroxylated toluenes. These compounds exhibit an even lower volatility, and due to steric hindrance their diffusion out of the zeolite pores seems to be very slow compared with the reaction rates of possible consecutive reactions [10,12,13,27]. Since the formation of those compounds cannot be excluded and no significant amounts were found during our experiments, we believe that they would stay on the zeolite acting as coke or coke precursors, if formed. Furthermore the formation of polycondensed aromatic rings and oxygenates during the conversion of toluene on H[Al]ZSM-5 in the presence of oxygen is well known from the literature [28,29]. The deactivation of H[Al]ZSM-5 during the hydroxylation of toluene with N_2O could thus be caused by both polyhydroxylated cresols and/or polycondensed aromatic rings. This explanation is supported by the observations for a rise of the reaction temperature from 450 to 500 °C with a molar excess of N_2O. The domination of the consecutive reactions for an excess of N_2O at higher temperatures can be seen from the selectivities to cresol shown in figure 4. At 400 °C a significant gain in selectivity, at higher conversions of toluene, was observed. Going to higher reaction temperatures only a slight increase in selectivity for sample A′ is found compared with a molar feed ratio of 1:1. Sample B′ exhibits even

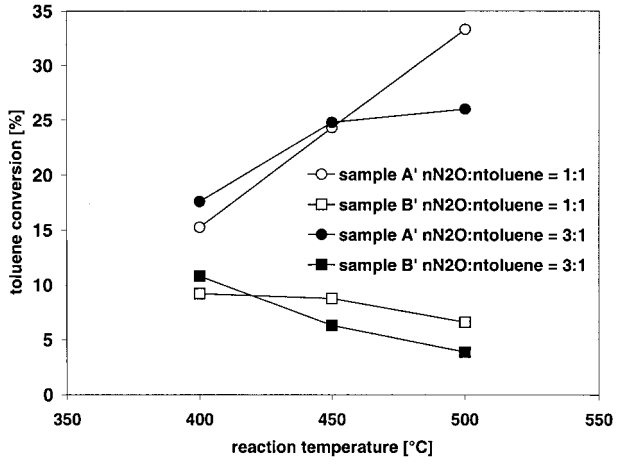

Figure 3. Toluene conversion *versus* the reaction temperature for a molar feed ratio of $n_{N_2O} : n_{toluene}$ of 1:1 and 3:1.

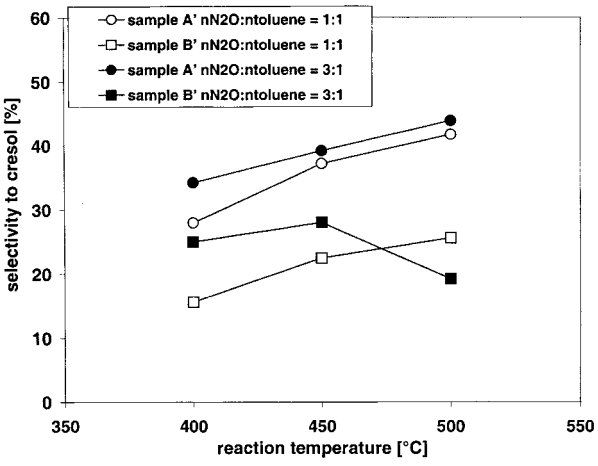

Figure 4. Selectivity to cresol *versus* the reaction temperature for a molar feed ratio of $n_{N_2O} : n_{toluene}$ of 1:1 and 3:1.

a lower selectivity to cresol at 500 °C than at 400 °C and 450 °C.

To reach high yields of the intermediate formed cresols, the relation between the diffusion of the cresols out of the pores and the reaction rate for the consecutive reactions has to be optimized. In other words, to realize a high macroscopic yield of cresol the diffusion of the primary formed cresols has to be faster than the consecutive reactions. Our findings discussed above indicate that the direct hydroxylation of toluene on H[Al]ZSM-5 exhibits a severe product diffusion limitation. This is in agreement with the observations of Guisnet *et al.* [27]. They found that the rapid deactivation of USHY during the alkylation of phenol with methanol was caused by limitations in diffusion of the reaction products (cresol and anisol) towards the outer surface of the zeolite crystal [27].

We want to further discuss the large differences between the two zeolites in terms of selectivity and toluene conversion after 15 min on stream. The parameters influencing the retention time of the cresols inside the pores of the hydroxylation catalyst can be described as the complex interaction between adsorption, diffusion, consecutive reactions, and the pore structure and acidity of the zeolite. As was shown by Parton *et al.* [11] for the alkylation of phenol with ethylene and by Klemm *et al.* [30] for the adsorption of phenol on H[Al]ZSM-5, strong interactions between the polar phenol molecules occur even on a rather hydrophobic zeolite like ZSM-5. In the case of a severe product diffusion limitation, the length of the diffusion path out of the zeolite pores and the acidity of the catalyst are suggested to be key issues concerning the macroscopic yield of cresol. The average crystal size for sample A′ in table 2 was determined to be 50 nm, whereas sample B′ has an average crystal size of 2 μm, revealing a difference of more than one order of magnitude. The slightly higher concentration of Brønsted acid sites determined for sample B′ may play a role in acid-catalysed reactions of the primary formed cresol, but it cannot be the only reason for the observed significant differences in toluene conversion, selectivity to cresol and deactivation.

Next to a short diffusion path for the desorbing cresol, the smaller crystals of sample A′ provide a large external surface area. The higher cresol yields for sample A′ could be due to the fact that the hydroxylation reaction mainly proceeds on the larger external surface of the small crystals. However, in the case of benzene, having the same kinetic diameter as toluene [31], it was shown by Piryutko *et al.* [32] and by Kharitonov *et al.* [33] that the hydroxylation reaction on FeZSM-5 proceeds primarily inside the zeolite channels. Thus it can be ruled out that a higher activity is caused by the larger external surface of sample A′.

Figure 5 shows the selectivity to cresol and the relative amount of para-cresol in the cresol fraction versus time-on-stream for a feed ratio of 1:1 and a reaction

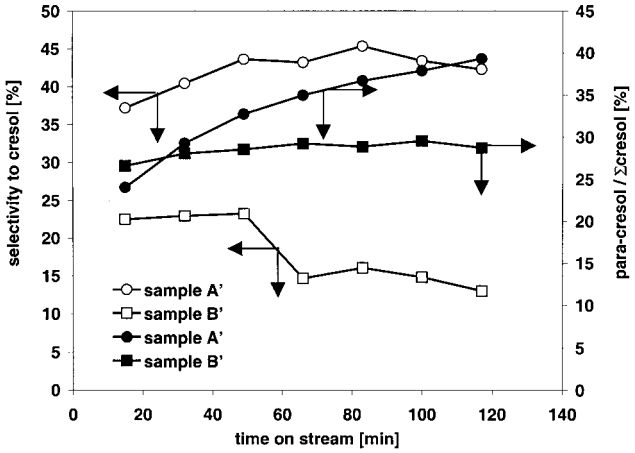

Figure 5. Selectivity to cresol and relative amount of para-cresol in the cresol fraction *versus* time on stream for a stoichiometric feed ratio at 450 °C.

temperature of 450 °C. The selectivity to cresol on sample B′ decreases with time on stream and increasing deactivation of the zeolite. For sample A′ an increase with time-on-stream is observed. The increase in selectivity to cresol with time-on-stream for the small crystals can be explained by the relatively short residence time of the polar cresols in the crystals, due to the reduced length of the diffusion path, and the decreasing consecutive reactions, due to the deactivation of the zeolite. Thus the rates of consecutive reactions become significantly lower compared with the diffusion rates and the intermediate selectivity to cresol increases.

The relative amount of para-cresol in the cresol fraction on sample B′ after 15 min on stream is found to be slightly higher than on sample A′. With time-on-stream a significant increase in para-cresol selectivity for the small crystals (sample A′) is observed, whereas sample B′, which is supposed to be the para-selective zeolite, exhibits no change of the relative amount of para-cresol with increasing reaction time.

The increase in para-selectivity is rather unusual for such small crystals, providing a short diffusion path. It could be explained by a decrease in internal and external isomerization activity. Thus a high para-cresol selectivity can be realized by the combination of a high primary formed para-cresol amount, a low isomerization rate and a short diffusion path.

3.4. Coke content

The amount of coke deposited after 134 min on stream on both zeolites was assigned to the weight loss after burning of the deposits between 500 °C and 900 °C in air. The total mass of coke per gram zeolite, the produced amount of cresol, and a normalized coke content after 134 min on stream are shown in figure 6. The normalized amount of coke is calculated by the mass of deposits divided by the mass of produced

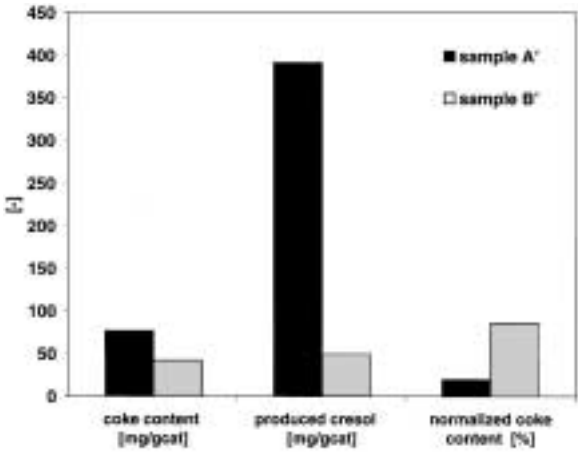

Figure 6. Coke content, produced amount of cresol and normalized coke content after 134 min on stream for a stoichiometric feed ratio at 450 °C.

cresol. The total mass of coke per gram zeolite is twice as high for zeolite A′ as for zeolite B′. This reveals that a higher amount of carbon is deposited on the zeolite having smaller crystals and a slightly lower acidity. However, the mass of produced cresol over 134 min on sample A′ is nearly ten times higher than on zeolite B′. A comparison of the normalized coke contents shows that the mass of coke formed on sample B′ per gram produced cresol is four times higher than on sample A′. This reveals that on sample A′ having smaller crystals a relatively lower amount of the primary products reacts further to form coke inside the zeolite pores.

4. Conclusions

The investigations have shown that for the synthesis of cresol via the direct hydroxylation of toluene with N_2O on H[Al]ZSM-5, a severe product diffusion limitation is found. The macroscopic cresol yields show a strong dependence on the molar feed ratio, the reaction temperature, and the crystal size of the zeolite. The selectivity to cresol and the conversion of toluene can be significantly enhanced with increasing temperature on H[Al]ZSM-5 having small crystals and a low level of acidity. The deposited mass of coke per gram produced cresol on the zeolite having smaller crystals and a slightly lower acidity.

A significantly higher para-xylene selectivity on the H[Al]ZSM-5 with larger crystal size is found whereas in the case of cresol, formed via the direct hydroxylation of toluene with N_2O, a higher para-cresol selectivity for the small crystals is observed.

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