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Microreaction engineering studies of the hydroxylation of benzene with nitrous oxide

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Abstract

Fe-ZSM-5 coated stainless-steel supports have been prepared by slurry coating technique using aluminium oxide as a binder and glacial acetic acid as the peptising agent. The zeolite-coated supports were characterised by means of XRD and N_2 adsorption measurements. The influence of the binder on the properties of the zeolite-coated supports such as surface area, micropore volume and adhesive strength was investigated. With coated stainless-steel supports the direct hydroxylation of benzene to phenol was performed in a microreactor. This allows to work at elevated initial temperatures and high concentrations of the reactants, thus high space–time yields can be achieved. The effects of temperature and concentration of nitrous oxide on the initial yield as well as on the deactivation behaviour were investigated in order to maximise the achievable yield over several hours time-on-stream.

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Keywords: Benzene; Nitrous oxide; Hydroxylation; Phenol; Coating; Fe-ZSM-5; Microreaction engineering/catalysis; DEMiS^{TM}

1. Introduction

Phenol and its derivatives are industrially important in the synthesis of many drugs, dyes and insecticides [1]. World-wide production of phenol is around 6 million tons annually. Traditionally phenol is produced mainly by the three-stage cumene process [2]. This process possesses some inherent disadvantages such as high investment costs, the hazardous intermediate cumene hydroperoxide and the formation of acetone as a co-product in a 1:1 stoichiometry (0.62 t/t phenol). If the market demand for acetone grows smaller than that of phenol, this process loses its profitability in the long run [3].

An alternative route for the production of phenol is the hydroxylation of benzene with nitrous oxide in the gas phase using ZSM-5 (MFI) type zeolites as catalysts (Fig. 1). In this one-step process phenol is obtained without a co-product. This reaction has been investigated for more than 20 years, usually in conventional fixed-bed reactors (e.g. reviews of Panov et al. [4] and Panov [5]). At 673 K the overall reaction enthalpy of the hydroxylation of benzene to phenol is $259\,\mathrm{kJ\,mol^{-1}}$, the enthalpies of undesired further oxidations of phenol are even higher. This high reaction enthalpy is due to the fact that on the one side benzene is oxidised to phenol (the difference in the enthalpies of benzene and phenol is $171\,\mathrm{kJ\,mol^{-1}}$) and on the other side the decomposition of N_2O supplying the oxygen for the hydroxylation generates further enthalpy ($\Delta H = 88\,\mathrm{kJ\,mol^{-1}}$). Considering only the reaction to phenol and not regarding consecutive reactions of phenol there is a release of energy of 2750 kJ per kg of phenol produced. Including the inevitable and also undesired consecutive oxidation of phenol to mainly dihydroxybenzene, benzochinone and carbon dioxide, the release of energy is even higher.

Using a reactor with a poor heat transfer out of the reactor, the release of energy from the hydroxylation reaction raises the reactor temperature significantly. Measurements with 8% N_2O and 8% benzene (rest: N_2) at $\tau_{\mathrm{mod}} = 93\,\mathrm{g\,min\,mol^{-1}}$ in a tubular reactor ($d_i = 17.4\,\mathrm{mm}$) resulted at a starting temperature of 673 K in an overall measured temperature raise of 60 K. At a starting temperature of 723 K, due to enhanced total oxidation of phenol the temperature raise is even higher. Furthermore high temperatures reduce the selectivity towards phenol. Working at a starting temperature of 723 K with a mixture of benzene and nitrous oxide of 1:1 in a laboratory tubular reactor the selectivity of nitrous oxide to phenol is typically only 30%—the rest of the N_2O oxidises phenol totally to carbon dioxide. In order to avoid high temperatures and to work at high selectivity, the tem-

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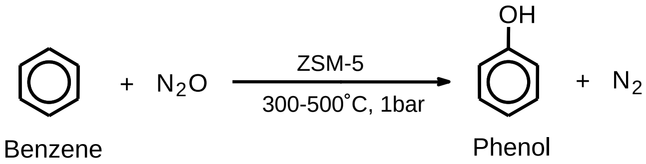

Fig. 1. One-step hydroxylation of benzene to phenol.

perature raise had to be limited by the amount of nitrous oxide added. As soon as all the N_2O has reacted there can be no further raise in temperature. However, these low amounts of N_2O cause a dilution of the reaction mixture leading to low space–time yields.

In order to improve heat and mass transfer, structured reactors with ZSM-5 coated on stainless-steel grids have also been used in the direct oxidation of benzene to phenol with very high selectivity of benzene to phenol [6,7]. In our work, we have coated Fe-ZSM-5 in microstructures with a hydraulic diameter of about 1 mm for catalytic measurements. The method for the catalyst preparation had been developed before on flat test supports. Using a microreactor with the ability to remove the heat directly from the catalyst to the wall of the reactor offers the possibility to conduct the hydroxylation of benzene under isothermal conditions. Since there is almost no temperature raise this allows to work at elevated initial temperatures and at high concentrations of the reactants without needing to dilute the reactants. As nitrous oxide and benzene can form explosive mixtures at high concentrations of N_2O [8], using a microreactor with inherent safety due to small dimensions offers furthermore the possibility to work at high concentrations of nitrous oxide leading to high space–time yields. Thus, the hydroxylation of benzene is an appropriate test reaction for Demonstration Project for the Evaluation of Microreaction Technology in Industrial Systems (DEMiS^{TM}). In this project the suitability of microreactors for an industrial scale production of bulk chemicals by heterogeneous gas phase catalysis is to be demonstrated. For this it was necessary on one hand to find suitable reactions fulfilling certain criteria and on the other hand to design, erect and operate a microreactor pilot plant. Simultaneously the former has been done at the university partners and the latter at the industry partners Degussa and Uhde.

2. Experimental

2.1. H-ZSM-5 and Fe-ZSM-5 coatings on stainless-steel test supports

H-ZSM-5 and Fe-ZSM-5 were prepared from Na-ZSM-5 (Si/Al = 40) by repeated ion-exchange with NH_4NO_3 and $FeCl_3$ solutions, respectively. The ion-exchange reactions were carried out at 343 K. Aluminium oxide (Condea, Germany) was used as a binder. Glacial acetic acid (100%) was purchased from Merck, Germany.

Preliminary coating experiments were conducted using a model catalyst (H-ZSM-5) with different amounts of Al_2O_3 binder in order to develop a useful coating procedure. The slurry used in the coating procedure was prepared according to the following procedure. At first, the MFI-type (H-ZSM-5 or Fe-ZSM-5, Si/Al ratio $\sim$ 40) zeolite was mixed with the required amount of Al_2O_3 binder. Glacial acetic acid solution was added as a peptising agent to the above mixture and the suspension was grinded thoroughly in a mortar. The ratio of zeolite (H-ZSM-5 or Fe-ZSM-5) to binder in the final slurry was 9:1 (wt.%). Prior to the zeolite (slurry) coating procedure, the stainless-steel supports were thoroughly cleaned with acetone and then dried at 373 K. The slurry was then placed on the stainless-steel support. The zeolite-coated support was dried at room temperature for 30 min, then the temperature was subsequently increased at a ramp rate of $10\,K\,min^{-1}$ to 373 K, held there for 30 min, then increased to 873 K in atmospheric air and maintained at this temperature for 12 h. No further pre-activation of the catalyst was needed prior to the reaction.

2.2. Characterisation

X-ray powder diffraction (XRD) measurements were carried out on a Philips X-ray diffractometer using Cu Kα radiation. All the samples were scanned in the 2θ range of 2–50° at a scan rate of $2^{\circ}\,min^{-1}$. The relative crystallinity of the Fe-ZSM-5 samples was determined from the sum of the areas of the peaks between $2\theta = 21^{\circ}$ and 25°. The BET surface areas and micropore volumes of the samples were determined by an automated nitrogen adsorption analyser (Micromeritics, ASAP 2010). The samples were out gassed at 200 °C for 3 h prior to adsorption.

2.3. Catalytic testing

The set-up consists of a lab-scale microreactor with the necessary dosage and analysis units. The reactor consists of a housing and replaceable microstructured internals. The internals were coated in a similar way to the technique described above. 0.86 g of Fe-ZSM-5 together with 0.09 g of Al_2O_3 was coated on an overall surface of about $20\,cm^2$. The hydraulic diameter of the coated microstructured internals is about 1 mm. Benzene was dosed with a liqui-flow and evaporated with nitrogen as carrier gas. Nitrous oxide and nitrogen were dosed with mass-flow controllers. Two gas chromatographs were used for the analysis of reactants and products. For the aromatics a Hewlett Packard 5890 GC with a HP-5 capillary column (length: 25 m; diameter: 0.31 mm; film thickness: 0.52 μm) with a flame ionisation detector (FID) was used. Nitrous oxide and carbon dioxide were measured with a microgas chromatograph from Chrompack (CP 2002P) equipped with a 12 m long PORA-Plot Q column and a thermal conductivity detector (TCD). Methane was used as internal standard for both GCs. Measurements were taken for every 15 min over a period of 4 h. The yield of phenol is directly calculated from the obtained amount of phenol and the selectivity of nitrous oxide toward phenol is defined as the molar ratio of the phenol obtained relative to nitrous oxide converted. The experiments were conducted at temperatures ranging from 673 to 773 K, with a fraction of benzene of 32% and fractions of nitrous oxide varying from 3.2 to 24% at a modified residence time of 40 g min mol^{-1}.

A mixture of oxygen and nitrogen (33% oxygen) dosed also with mass-flow controllers was used for regeneration. The catalyst was regenerated at 815 K for less than 2 h restoring the initial activity.

3. Results and discussion

3.1. H-ZSM-5 and Fe-ZSM-5 coatings on stainless-steel test supports

In preliminary experiments H-ZSM-5 samples mixed with different amounts (0–20 wt.%) of binder were coated on the stainless-steel test supports as shown in Fig. 2. The dark parts indicate where the zeolite did not bind to the stainless-steel support. In the absence of a binder (Fig. 2a), the zeolite coating was very poor. Most of the zeolite catalyst peeled off the test support. Using 5 wt.% of binder considerably improved the binding of the zeolite on the support but did not lead to satisfactory results as there are still small visible parts without catalyst (Fig. 2b). It can be seen from Fig. 2c and d, that 10–20 wt.% of binder is necessary for successful coating of H-ZSM-5 on the test stainless-steel supports. These supports are completely covered with catalyst without any visible cracks. The textural properties and the adhesive strength of the coated supports are summarised in Table 1. The binder-free H-ZSM-5 sample has a high surface area (375 m^2 g^{-1}) and micropore volume (0.17 cm^3 g^{-1}). However, no adhesive strength was observed. As the amount of binder increases the BET surface areas and micropore volume decreases gradually. Note that the adhesive strength of the H-ZSM-5 sample mixed with 10 wt.% aluminium oxide is quite high (40 N cm^{-2}). Furthermore, there was no significant increase in the adhesive strength for the H-ZSM-5 sample mixed with 20 wt.% of aluminium oxide (42 N cm^{-2}). Therefore, we chose to carry out the Fe-ZSM-5 (Si/Al ratio = 40, iron content = 0.23 wt.% Fe_2O_3) coatings with 10% of aluminium oxide for our further studies. This Fe-ZSM-5 zeolite catalyst has proven to be an appropriate catalyst for this reaction in previous investigations [9].

Table 1
Properties of zeolite-coated supports

Sample	BET surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Adhesive strength (N cm^{-2})[a]
H-ZSM-5	375	0.17	–[b]
H-ZSM-5 + 5% Al_2O_3	354	0.15	12
H-ZSM-5 + 10% Al_2O_3	351	0.15	40
H-ZSM-5 + 20% Al_2O_3	311	0.12	42
Fe-ZSM-5	318	0.13	–[b]
Fe-ZSM-5 + 10% Al_2O_3	309	0.12	39

[a] Determined by adhesive tape technique.
[b] No adhesive strength observed.

The N_2 adsorption isotherms of the pure Fe-ZSM-5 and the Fe-ZSM-5/Al_2O_3 coated on the stainless-steel test support are shown in Fig. 3. As expected, the N_2 adsorption isotherms show type I isotherms, which are characteristic of microporous materials. Moreover, the isotherms did show no observable difference. The Fe-ZSM-5 sample has a surface area of 318 m^2 g^{-1} and micropore volume of 0.13 cm^3 g^{-1}. However, a slight decrease in surface area (309 m^2 g^{-1}) and micropore volume (0.12 cm^3 g^{-1}) is observed for the Fe-ZSM-5/Al_2O_3 sample coated on the test support. Fig. 4 shows the typical XRD patterns of the pure Fe-ZSM-5 and the Fe-ZSM-5/Al_2O_3 sample coated on the stainless-steel test support. The XRD patterns of the Fe-ZSM-5 matched well with the pattern reported in [10], indicating the material is free from impurities. This sample was considered to be 100% crystalline. We note that the XRD pattern of the Fe-ZSM-5 coated on test support exhibits less intense peaks although there was no change in the position of the peaks. The calculated crystallinity of the Fe-ZSM-5 sample coated on the stainless-steel test support (95%) was slightly lower than that of the parent Fe-ZSM-5 (100%). This could be due to the presence of binder which is amorphous in nature.

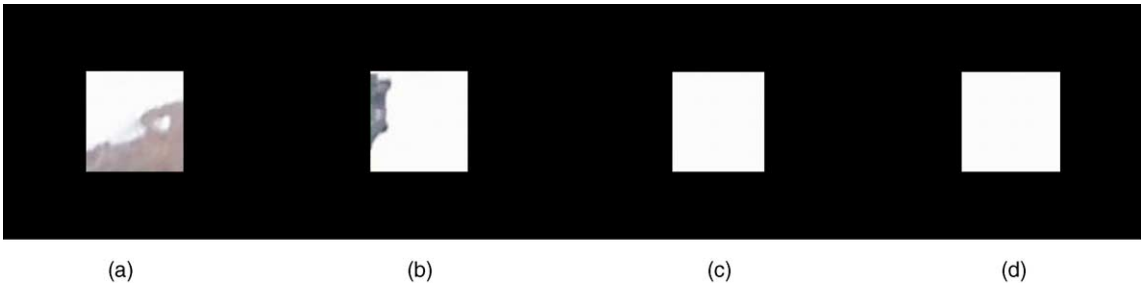

Fig. 2. Coating experiments of H-ZSM-5 on stainless-steel test supports (2 cm × 2 cm) with different amounts of binder: (a) H-ZSM-5 without binder; (b) H-ZSM-5 with 5% Al_2O_3; (c) H-ZSM-5 with 10% Al_2O_3; (d) H-ZSM-5 with 20% Al_2O_3.

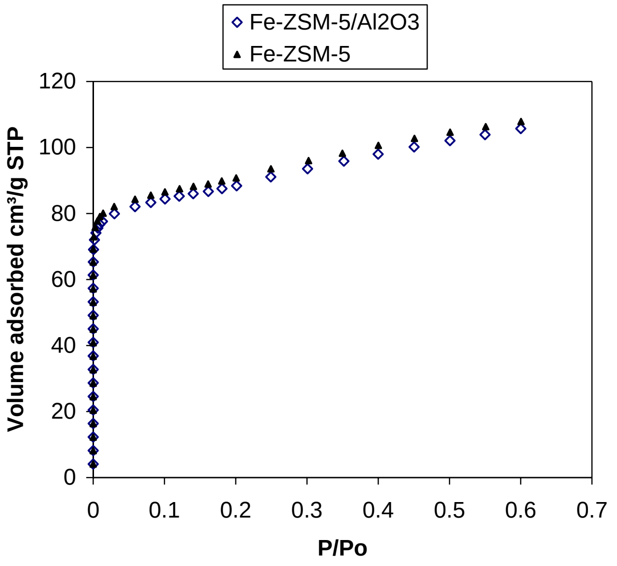

Fig. 3. N_2 adsorption isotherms of pure Fe-ZSM-5 and the Fe-ZSM-5/Al_2O_3 sample coated on stainless-steel test support.

3.2. Hydroxylation of benzene to phenol

The above-described technique was used for coating Fe-ZSM-5 on microreactor supports. Thus, it was possible to conduct catalytic measurements in a microreactor. Within the scope of the DEMiS^{TM}-project, the objective was to reach space–time yields of 1.5 kg phenol per kg catalyst and hour with a selectivity of the oxidising agent N_2O towards phenol of at least 50%, preferably for 36 h time-on-stream. As reported by Renken and coworkers [7] raising the benzene concentrations increases the selectivity towards phenol. This is consistent with results reported by Kustov et al. [11] and also with previous works of Emig and coworkers [12], assuming that an excess of benzene reduces the adsorbed amount of phenol on the sites and therefore reduces the possibility of further hydroxylation of phenol. Recent kinetic measurements of the hydroxylation of benzene with N_2O also showed that there is competitive sorption of benzene and phenol [13].

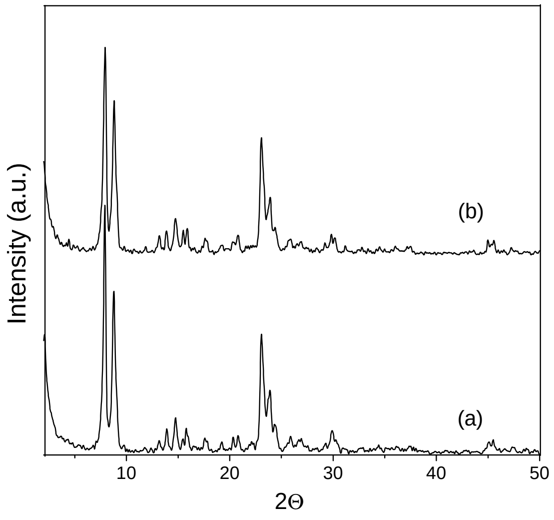

Fig. 4. XRD patterns of: (a) pure Fe-ZSM-5 and (b) Fe-ZSM-5/Al_2O_3 sample coated on stainless-steel test support.

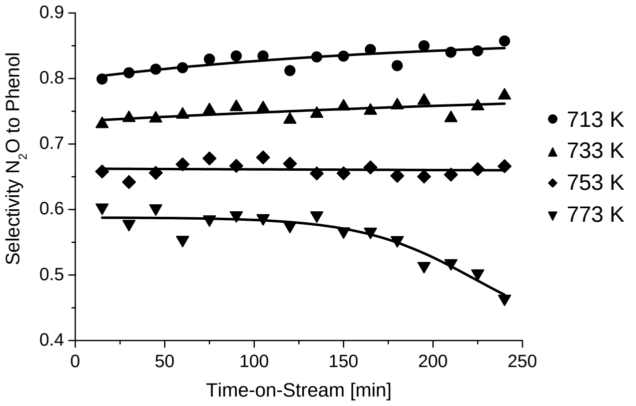

Fig. 5. Selectivity of nitrous oxide toward phenol at different temperatures with a mixture of 8% N_2O with a four-fold excess of benzene (32% benzene) ($\tau_{mod} = 40\,\mathrm{g\,min\,mol^{-1}}$).

Fig. 5 displays the selectivity of nitrous oxide to phenol in the temperature range of 713–773 K at mixtures of 8% N_2O with a four-fold excess of benzene at $\tau_{mod} = 40\,\mathrm{g\,min\,mol^{-1}}$ (rest: N_2) for a period of 4 h. First of all, the required selectivity of 50% is clearly achieved at 713, 733 and 753 K. At these three temperatures, the selectivity remains constant over a period of 4 h. At 773 K the selectivity is above the desired level except for the last measurement at 4 h time-on-stream due to a decrease over time which is presumably caused by the oxidation of coke formed in the zeolite as side reaction of the hydroxylation of benzene. The temperature was measured with a thermocouple directly at the catalyst bed—the raise in temperature was less than 5 K, independent of the position along the coated support. This raise is clearly below the adiabatic temperature rise. The selectivity of nitrous oxide to phenol is strongly reduced at high temperature due to further oxidation of phenol. Thus, using a microreactor in place of a tubular reactor increases the selectivity of nitrous oxide to phenol for not having hot spots or a temperature rise along the reactor. The observed selectivity with a microreactor is more than twice the selectivity achieved in the tubular reactor at a starting temperature of around 723 K.

As shown in Fig. 6, space–time yields of several kg phenol per kg catalyst and hour, even more than the required yield 1.5 kg phenol per kg catalyst and hour for the project can be achieved. Increasing the N_2O to benzene ratio clearly increases the space–time yield, however, the long-term stability is strongly reduced. Whereas there is only a slight decrease with time in the yield with the dosage of 4% of N_2O, the yield of phenol decreases strongly with increasing N_2O to benzene ratio (from 0.125 to 0.75). After only 2 h time-on-stream, the yields of phenol at 4 and 24% of N_2O are equal. High addition of nitrous oxide does not only favour the main reaction but also consecutive reactions. This

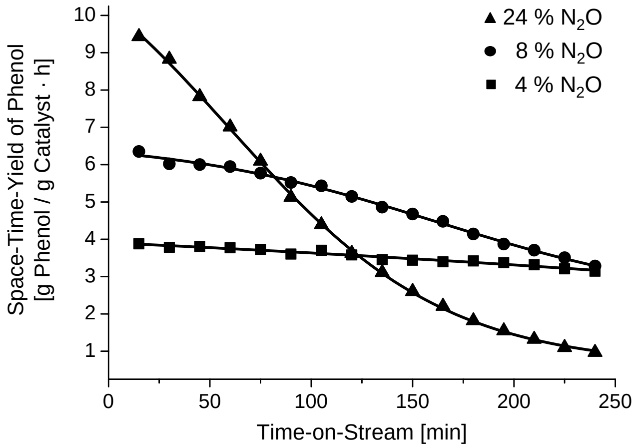

Fig. 6. Space–time yield of phenol displayed over time-on-stream at 32% benzene; 4, 8 respectively 24% N_2O ($\tau_{mod} = 40\,g\,min\,mol^{-1}$) at a temperature of 753 K.

leads to more coking of the catalyst which then causes a faster deactivation of the catalyst, corresponding with the decrease in selectivity of N_2O to phenol from 80% at 4% N_2O to below 50% at 24% N_2O. A reaction mixture of 32% benzene with 4% N_2O leads to an eight-fold excess of benzene. Thus slightly more than 10% of the dosed benzene is converted. Like the yield of phenol (Fig. 6), the conversion of benzene remains almost constant over the period of 4 h at these conditions. Doubling the amount of nitrous oxide added, a doubled conversion of benzene of almost 20% is detected. Due to deactivation the conversion drops to 10% after 4 h. At high dosage of N_2O a strong deactivation causes a severe decrease in the conversion of benzene. The initial conversion of 30% is reduced to one-tenth of its initial value after 4 h. This corresponds with the decrease in the yield of phenol (Fig. 6) and indicates a constant selectivity.

Besides adding more nitrous oxide, raising the reaction temperature offers another possibility to increase the yield of phenol. Fig. 7 shows the space–time yield of phenol at 32% of benzene and 8% of N_2O ($\tau_{mod} = 40\,g\,min\,mol^{-1}$) at various temperatures. There is an increase in the yield clearly up to 753 K. A further increase in the reaction temperature to 773 K yields almost the same amount of phenol as at 753 K at the beginning, but due to higher deactivation, the yield decreases faster compared to other temperatures. Furthermore, the selectivity towards phenol decreases as already shown in Fig. 5 due to the loss in the yield of phenol at 773 K. A further increase of the temperature favours the total oxidation of benzene and phenol leading to lower selectivity and therefore lower yield of phenol. So the temperature with the maximum output of phenol is expected to be between 753 and 773 K. As seen in Fig. 6, raising the addition of N_2O elevates the yield of phenol in the beginning. As an increasing N_2O content also favours the deactivation leading to lower yield of phenol, it is quite desirable to add only low contents of N_2O, therefore prolonging the reaction cycle before regeneration of the catalyst by burning off the deposited coke with oxygen at elevated temperatures.

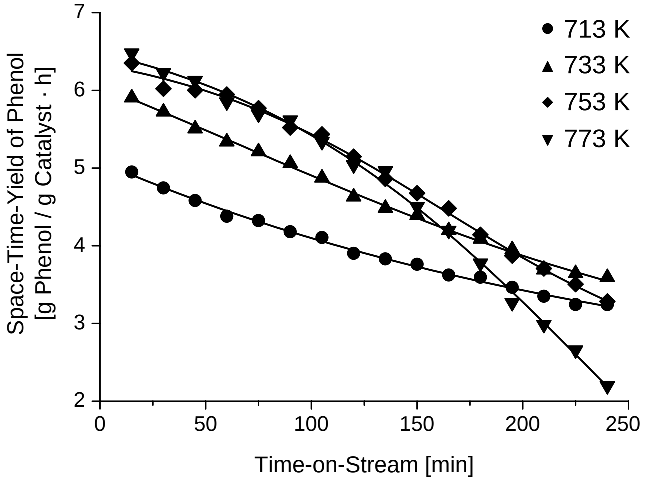

Fig. 7. Space–time yield of phenol at 32% of benzene and 8% of N_2O ($\tau_{mod} = 40\,g\,min\,mol^{-1}$) at different temperatures.

For industrial production it is necessary to operate at a high yield of the desired product for long periods, thus low deactivation is required. Fig. 8 shows the deactivation calculated as the relative decrease of the yield of phenol after 4 h time-on-stream related to the yield at 15 min time-on-stream (TOS). The decrease of the yield is plotted as a function of the initial yield (at 15 min TOS). As can be seen, the deactivation generally increases with increasing initial yield. This is not surprising since phenol is assumed to be the coke precursor, so deactivation caused by the deposition of coke increases with formation of phenol. However, as seen at yields of 3–4 kg phenol per kg catalyst and hour at 15 min TOS, the decrease in the yield varies from roughly 10% to almost 40%. To gain the desired yields working at low N_2O contents and high temperature leads to lower deactivation

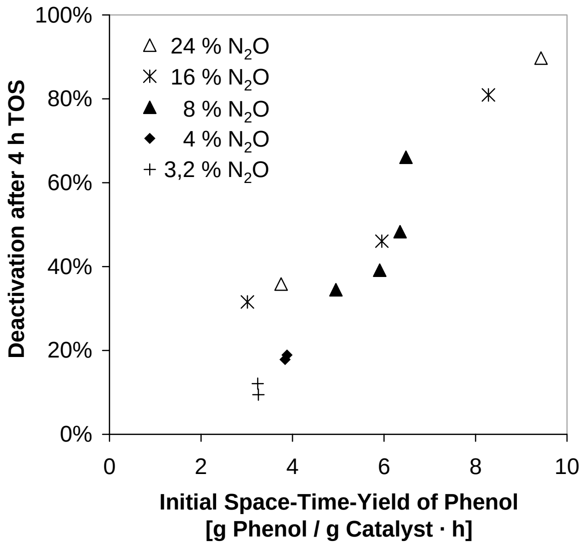

Fig. 8. Deactivation plotted via the initial space–time yield at different N_2O contents.

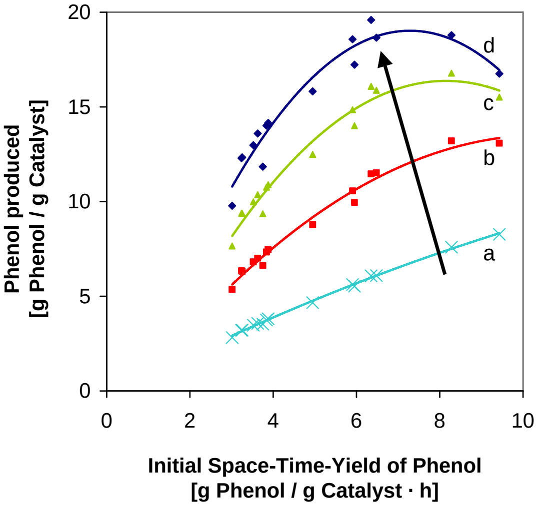

Fig. 9. Amount of phenol produced plotted via the initial space–time yield: (a) after 1 h time-on-stream; (b) after 2 h time-on-stream; (c) after 3 h time-on-stream; (d) after 4 h time-on-stream.

(decrease of about 10%) than working at high N_2O contents and lower temperatures (decrease of almost 40%).

Comparing the yields of phenol in Fig. 6 at 4% N_2O and 24% N_2O shows that starting with a high yield of phenol does not necessarily achieve more phenol over a long period. After 2 h time-on-stream the yield of phenol for 4% N_2O is higher than the yield for 24% N_2O. Fig. 9 illustrates the production of phenol plotted as function of the initial yield. There are four curves plotted for the amount of phenol produced during the first 1 h up to the first 4 h. These experiments were performed at temperatures ranging from 673 to 773 K with 32% benzene and 3.2 to 24% N_2O resulting in different yields at 15 min TOS plotted on the abscissa. The results of a single experiment can be seen by going straight upwards in the plot. The starting yield is always the same but the cumulative yield increases with time. Whereas the cumulative yield of phenol after 1 h can still be interpreted as straight line, the yields at longer duration are concave curves with the maximum shifting towards smaller initial yields as indicated by the black arrow. Conditions with low initial yields resulting in fewer deactivation maximise the cumulative yield for long-term periods.

4. Conclusions

ZSM-5 catalysts (H-ZSM-5 and Fe-ZSM-5) were coated effectively on stainless-steel test supports by slurry coating technique using aluminium oxide (10%) as a binder and glacial acetic acid as the peptising agent. It has been shown that the binder (10% Al_2O_3) is necessary for the effective coating of ZSM-5 on the test support. Using this coating technique, the hydroxylation of benzene with nitrous oxide can be performed in a microreactor. Exploiting the advantages of microreactors, these experiments can be performed at isothermal conditions and high concentrations of N_2O leading to space–time yields of several kg phenol per kg catalyst and hour. Due to the isothermal conditions in the microreactor, the selectivity was higher than in a tubular reactor, exceeding 50% selectivity of N_2O to phenol. Nevertheless due to coking the catalysts deactivates, so further investigations are needed to improve the long-term stability. Furthermore, using a microreactor allows isothermal kinetic measurements in a reactor similar to the one used for future production. Kinetic measurements were performed and the modelling of the kinetics is under current investigation.

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References

[1] Ullmann’s Encyclopedia of Industrial Chemistry, Phenol, CD-ROM, Wiley/VCH, Weinheim, 2003.
[2] K. Weissermel, H.-J. Arpe, Industrielle Organische Chemie, Wiley/VCH, Weinheim, 1998.
[3] W. Kleinloh, Proceedings of the First ICIS-LOR World Phenol/Acetone Conference, Antwerpen, 2000.
[4] G.I. Panov, A.K. Uriate, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1988) 365.
[5] G.I. Panov, CATTECH 4 (1) (2000) 18.
[6] B. Louis, P. Reuse, L. Kiwi-Minsker, A. Renken, Appl. Catal. A 210 (2001) 103.
[7] B. Louis, L. Kiwi-Minsker, P. Reuse, A. Renken, Ind. Eng. Chem. Res. 40 (2001) 1454.
[8] A. Uriate, Patent WO 98/15514 (1998).
[9] A. Reitzmann, Dissertation, Universität Erlangen-Nürnberg, 2001, ISBN 3-8265-9377-4.
[10] P. Ratnasamy, R. Kumar, Catal. Today 9 (1991) 329.
[11] L.M. Kustov, V.I. Bogdan, V.B. Kazansky, EP 0 889 018 A1 (1999).
[12] M. Häfele, A. Reitzmann, D. Roppelt, G. Emig, Appl. Catal. A 150 (1997) 153.
[13] A. Reitzmann, E. Klemm, G. Emig, Chem. Eng. J. 90 (2002) 149.