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Hydroxylation of benzene to phenol using nitrous oxide

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Abstract: There is an increasing commercial interest in finding alternative ways to produce phenol that overcome the disadvantages of the current cumene process used to synthesise phenol. The drivers for the change are both economical and environmental. A direct oxidation route for producing phenol from benzene is based on using N_2O as an oxidizing agent in the gas phase in the presence of modified Fe-ZSM5 zeolite. A series of selective Fe-ZSM5 catalysts with different Si/Al ratios have been prepared and evaluated for selective formation of phenol. Catalysts synthesized with high Si/Al ratios (80) and with low iron content (35mg/g) showed good long term stability (reduced deactivation rates) and demonstrated good phenol selectivity and reaction rates (6 mmol/g.h). Catalysts with high amounts of iron (~500mg/g) showed considerable deactivation particularly at high reaction temperatures (450°C). High reaction temperatures (450°C) in comparison with 350°C were found to favour higher reaction rates however, catalysts with high iron content were particularly prone to deactivation at this temperature.

Introduction

Worldwide production of phenol via the cumene process is around 11 million tonnes annually (Zakoshansky, 2009). Phenol is industrially important as a key intermediate for the production of bis-phenol A and phenolic resins (Schmidt, 2005). More than 90% of the world's phenol production technology is currently based on the cumene hydroperoxide route (Liptakova *et al*., 2004). Cumene is manufactured through the alkylation of benzene with propylene over an acid catalyst. The cumene produced is further oxidised (in air) to cumene hydroperoxide followed by acid catalysed decomposition to phenol and acetone. The co-production of acetone influences the process economics. The annual growth rate for phenol has not been matched by a similar increase in demand for acetone. There is concern that supply of acetone may exceed demand. The process economics of the cumene process significantly depends on the marketability of the acetone by-product (Kleinloh, 2000). Hence alternatives to the cumene process such as the gas phase direct oxidation of benzene (over zeolite catalysts e.g. ZSM-5) by nitrous oxide (N_2O) are of research interest. N_2O is a waste by-product of the adipic acid manufacturing process and is therefore an ideal source. It must otherwise be disposed of as a waste stream by conversion first to nitric oxide and then nitric acid (Schmidt, 2005). Currently, there is research interest in utilizing iron-based ZSM-5 catalysts for the process. This reaction has been investigated previously (Panov *et al*., 1988; Panov, 2000; Notte, 2000) who have reported that Bronsted acidity and the presence of α-sites linked to iron in the extra-framework positions are necessary. The current paper examines the effect of different Si/Al ratios and iron content on the selective conversion of benzene to phenol with a desire to achieve high selectivity and minimise catalyst deactivation.

Experimental Materials and Methods

Catalyst Preparation

ZSM-5 with different Si/Al ratios (30 and 80) were procured in Na form, from Zeolyst International USA. Fe/ZSM-5 samples (varying iron content, 0.1% or 1% by weight) were prepared by ion exchanging the Na^+ with Fe^{3+} using the method of Louis *et al*, (2001). Table 1 provides details of the samples prepared for the study.

Table 1. Nomenclature identifying catalyst samples prepared using ion exchange.

Fe / ZSM-5 catalyst			
Si / Al ratio (30)		Si / Al ratio (80)	
[FeZ30- 0.1%]	[FeZ30- 1%]	[FeZ80- 0.1%]	[FeZ80- 1%]
1	2	3	4

The preparation steps were as follows:

10g of the zeolite Na-ZSM-5 (30 or 80 - Si/Al) was mixed with 40ml of 0.1M NH_4Cl in a 100ml volume beaker. The mixture was heated at 80^oC using a heating plate equipped with a magnetic stirrer for 5h followed by filtration of the solid phase using a 0.1 µm cellulose filter. 40ml of NH_4Cl was added to the sample after filtration, and the mixture was heated at 80^oC for 5 h (with agitation at 450 rpm), and the sample was filtered again. This process was repeated one more time. The filtered catalyst was washed with distilled water for 45 minutes (in a sintered glass column) to remove any residual NH_4Cl. The sample with then air dried in an oven at 120^oC for 2 h. The sample was calcined by heating in an oven at 550^oC (CARBOLITE furnace) for 5 h to convert the sample to form H-ZSM-5.

10 g of the zeolite H/ZSM-5 (30 or 80 - Si/Al) was mixed with a known volume of 0.2M $Fe(NO_3)_3$ (98% purity) in a 100ml volume beaker. The mixture was heated at 50^oC using a heating plate equipped with a magnetic stirrer for 10h followed by filtration of the solid phase using a 0.1 µm cellulose filter. A known volume of 0.2M $Fe(NO_3)_3$ (98% purity) was added to the sample after filtration, and the mixture was heated to 50^oC and kept at this temperature for 10 h (with agitation at 450 rpm) and then filtered again. This process was repeated a second time. The filtered catalyst was washed with distilled water for 45 minutes to remove any residual Fe $(NO_3)_3$. The sample with then dried in an oven at 120^oC for 2.5h. The sample was calcined by heating in air in an oven at 900^oC for 15 h to activate the sample.

*Catalyst **Characterisation***

*Elementary composition and surface area measurements*
Samples with different Si/Al ratios were digested overnight at room temperature using a concentrated mixture of HCl and HNO_3 (ratio 3:1vol%) . Boiled gently under reflux for 2 h before dilution and analysis by a Varian Atomic Absorption Spectrophotometer (AAS). The elementary compositions (Si, Al, Fe and Na content) of the ZSM-5 catalysts were determined. The surface area and pore volume of the samples were measured by nitrogen adsorption at 77K using a Micrometrics ASAP 2010 analyzer.

Particle size distribution

Particle size measurements were carried out using a Malvern mastersizer. Malvern has a range of particle size measurement solutions from 100 nm to 900 μm in size.

Experimental setup to evaluate catalyst performance

The experimental rig consists of a gas handling system (see Figure 1) to produce mixtures of N_2O and benzene in a stream of helium. The gas mixture if fed to a packed bed reactor (PBR) containing a known quantity of the catalyst. The reactor feed and exit gas streams are sampled and analyzed using an on-line gas chromatography (GC) unit. The GC capillary column used is a DB-1701.
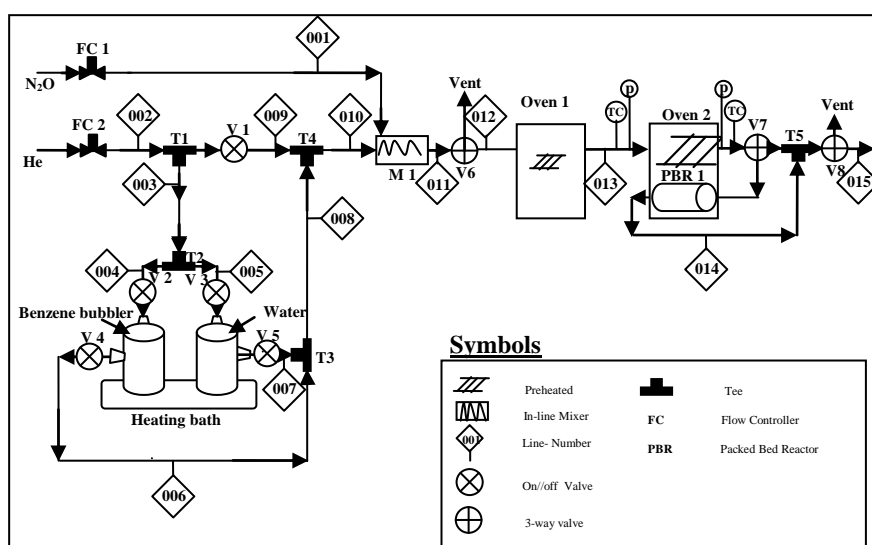
Figure 1. Line diagram of the packed bed reactor (PBR) system.

Catalyst performance was evaluate using the experimental packed bed reactor (PBR). For each experiment, 200 mg of 0.1–0.2 mm diameter catalyst particles were placed into a stainless steel reactor with an inner tube diameter of 2 mm. The feed gas composition was varied using different flow rates of helium and N_2O regulated using mass flow controllers (MFC). The benzene feed rate was influenced by the flow of helium gas through the benzene bubbler equilibrated at 50°C. The reactor feed and exit gas mixtures were sampled and analyzed on-line. The effect of reaction temperature at 350°C and 450°C was studied. The feed gas contained 7 mol% N_2O and the rest was a mixture of benzene/helium. The total flow rate exiting the reactor was 60 ml/min. Catalyst experiments were performed using Fe/ZSM-5 (0.1 and 1 % w/w) with a feed gas containing 10 ml/min N_2O, 50 ml/min Benzene/He. Samples were collected every hour during the 20 h of reactor operation. The catalysts were tested using a feed containing an excess of nitrous oxide in comparison with benzene (~1 mol% benzene compared with 7 mol% N2O). The reaction temperature of 450°C was chosen as a reference temperature, because the majority of the data available in literature is given for this reaction temperature. In addition, this reaction temperature represents a good compromise between the activity of the catalyst and the deactivation rate.

## Results and discussion

Elementary composition

The elemental composition data for the different catalyst samples are shown in Table 2 (below).

Table 2. Elemental composition of samples determined using AAS.

| Catalysts	Na content (mg/g cat)	Al content (mg/g cat)	Si content (mg/g cat)	Fe content (mg/g cat)
Na -ZSM-5 30	0.44 ± 0.02	-	-	<1
Na -ZSM-5 80	0.39 ± 0.01	-	-	<1
[0.1% Fe-Z30]	0.51 ± 0.01	25.2 ± 0.5	12.2 ± 9.4	35
[1% Fe-Z30]	0.15 ± 0.02	9.0 ± 0.7	23.8 ± 6.6	446
[0.1% Fe-Z80]	0.16 ± 0.01	14.8 ± 2.5	62.5 ± 7.7	34
[1% Fe-Z80]	0.30 ± 0.01	9.0 ± 0.2	25.3 ± 11.6	641

Particle size distribution

The Na-ZSM-5 catalyst supplied by Zeolyst International was in the size range (0.1 – 10 µm). The mean particle size by volume for the sample was 2.9 µm and the sauter mean diameter was 0.75 µm. The mean particle size by volume for the sample after pelleting and grinding was 154 µm and the sauter mean diameter was 33 µm. Figure 2 shows that the cumulative particle size distribution of Fe/ZSM-5.
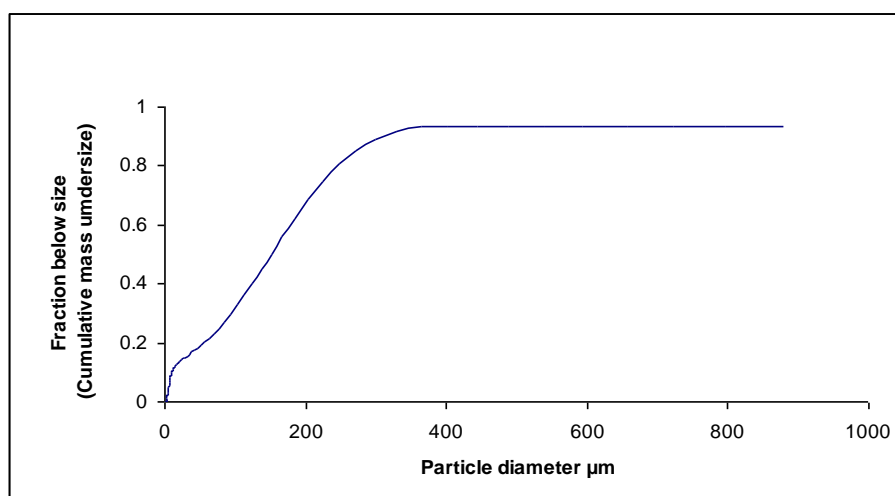
Figure 2. Cumulative particle size distribution of Fe/ZSM-5.

Surface area measurements

The surface area and pore volume of the catalyst samples were investigated by nitrogen porosimetry. The total surface area and the pore volume for the Na-ZSM-5 (Si/Al ratio, 30) catalyst before catalyst pretreatment (pelleting, grinding and conversion to iron form) were 338 m^2 g^{-1} and 0.23 cm^3 g^{-1}. After sample pretreatment the area and pore volume were almost unchanged at 334 m^2 g^{-1} and 0.22 cm^3 g^{-1}. Figure 3 shows that the adsorption isotherms for the samples Na-ZSM-5 (Si/Al ratio, 30) catalyst before and following the preparation of Fe/ZSM-5.
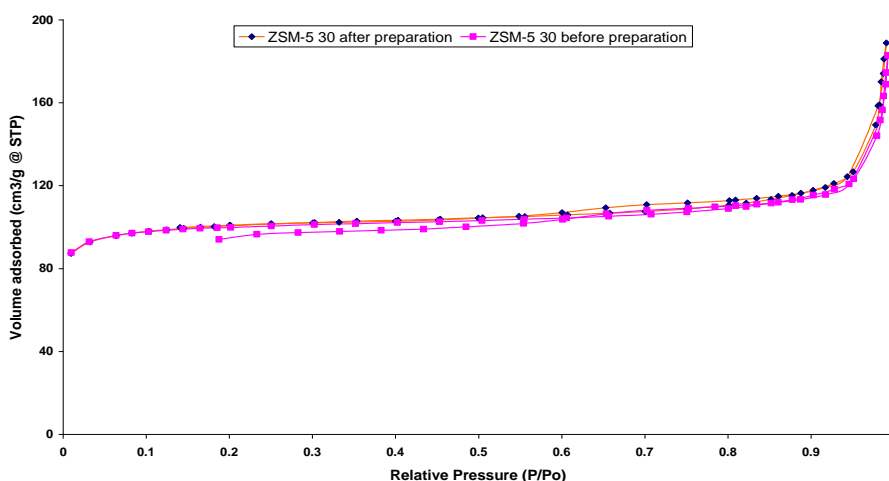
Figure 3. Catalyst characterisation using nitrogen porosimetry.

Phenol production using Fe-ZSM-5 catalysts

The stability of the feed composition as a function of time was evaluated (see Figure 4). The flow rate of N_2O was set at 10 ml/min and that of helium fed through a benzene bubbler (bubbler temperature set at 50°C) was 50 ml/min. The feed preheater temperature was set at 300°C and the reactor temperature was set at 450°C. The sampled feed composition was found to be steady over the duration of the experiment.
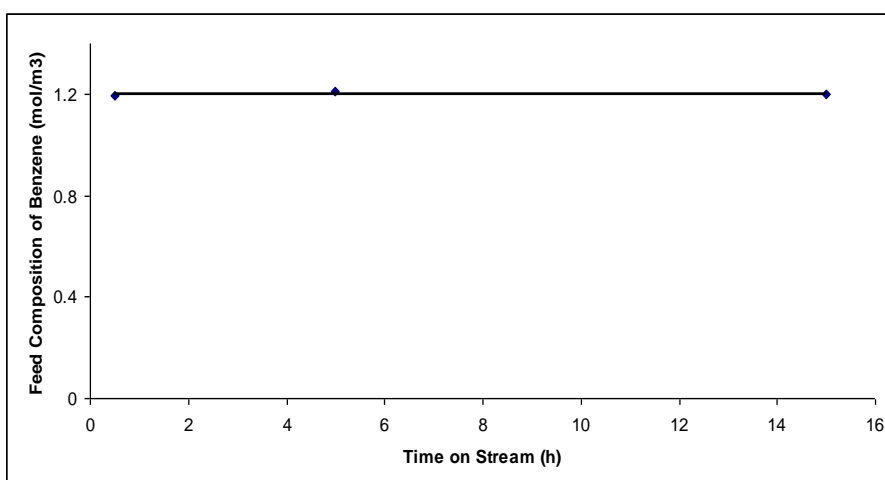
Figure 4. The stability of the feed composition of benzene as a function of time.

Effect of Iron content on phenol productivity

For samples Z30 the initial rate of phenol production was higher (see Figure 5) at 450°C (11.5 mmol /g. h) compared with 350°C (about 8.5 mmol /g. h). All samples showed considerable deactivation within the first 5 hours with concomitant decrease in the rate of phenol production. However, catalyst samples with lower iron content (35mg/g) showed a lower tendency to deactivate in comparison with the samples with higher iron content (~500mg/g). The 0.1% Fe sample at 450 °C shows higher initial phenol production (11.4 mmol /g. h), this production rate remains nearly constant for the first two hours of time on stream and then decrease to 6 mmol /g. h at 5 h. The productivity thereafter remains nearly constant between 5h and 20h on stream at this value. In comparison, the initial production rate of phenol for this sample (0.1%Fe/Z30) at 350 °C is about 7 mmol /g. h and the production rate decreases to about 4.2 mmol /g. h after the intial period of deactivation (lasting again around 5h). The 1%Fe/Z30 sample shows similar behaviour except the degree of deactivation at 450°C is markedly more severe (see Figure 5). It appears that the amount of iron in the sample affects the degree of deactivation. For catalyst samples with Si/Al ratio 30 lower iron content and high reaction temperature favour higher reaction rates and reduced tendency for catalyst deactivation.
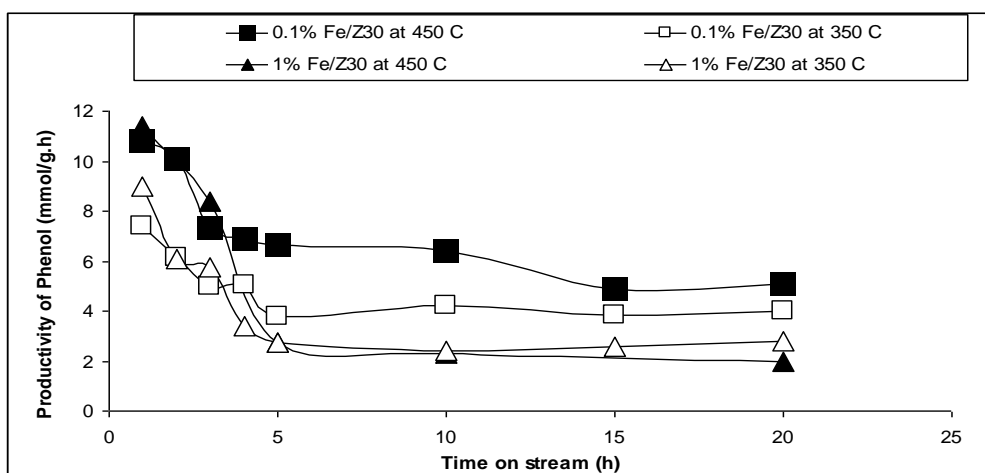

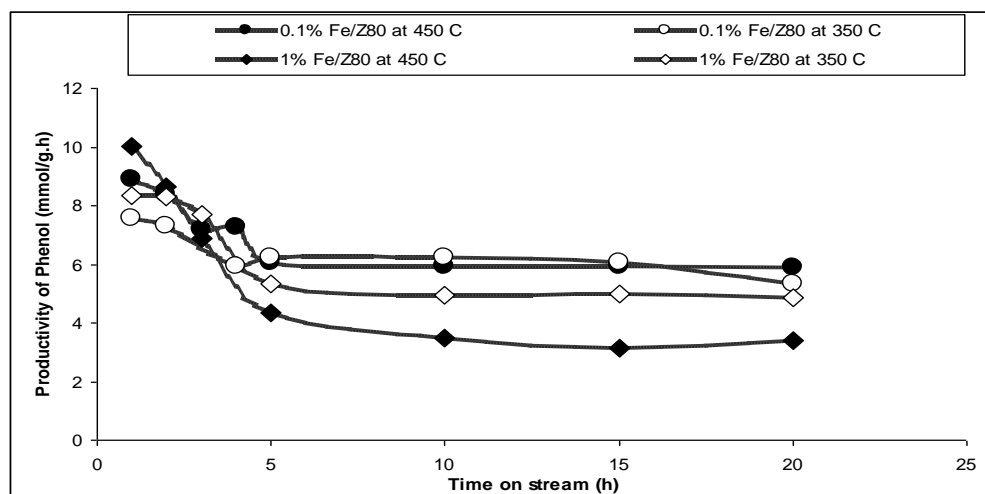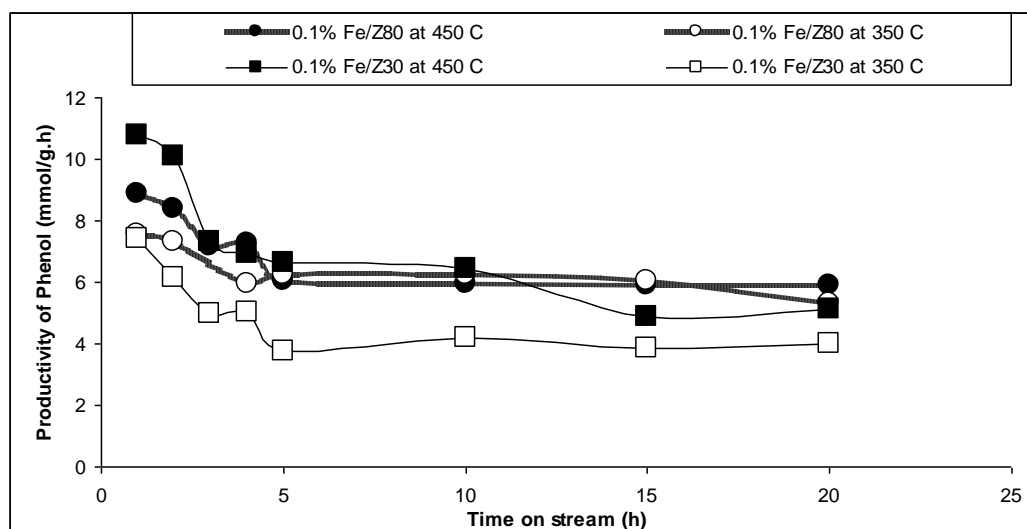**Figure 5**. Phenol productivities *vs* time on stream using Si/Al ratio 30.

Figure 6. Phenol productivities *vs* time on stream using Si/Al ratio 80.

6

For samples Z80 the initial rate of phenol production was higher (see Figure 6) at 450°C (~10 mmol /g. h) for 1%Fe/Z80 compared with 350°C (about 8 mmol /g. h). All samples showed considerable deactivation within the first 5 hours with concomitant decrease in the rate of phenol production. However, catalyst samples with lower iron content (~35mg/g) showed a lower tendency to deactivate in comparison with the samples with higher iron content (~500mg/g). The 0.1% Fe sample at 450 °C shows higher initial phenol production (~9 mmol /g. h), this production rate decreases to 6 mmol /g. h at 5 h. The productivity thereafter remains nearly constant between 5h and 20h on stream at this value. In comparison, the initial production rate of phenol for this sample (0.1%Fe/Z80) at 350 °C is slightly below about 8 mmol /g. h and the production rate decreases to slightly above 6 mmol /g. h at 5 h after the intial period of deactivation (lasting again around 5h). The 1%Fe/Z80 sample shows similar behaviour except the degree of deactivation at 450°C is markedly more severe (see Figure 5) and the post 5h production rate is less than 4 mmol /g. h. It appears again that the amount of iron in the sample affects the degree of deactivation. For catalyst samples with Si/Al ratio 80 lower iron content and a high reaction temperature favour higher reaction rates and reduced tendency for catalyst deactivation, however, unlike Si/Al ratio 30 the effect of temperature between 5-20h is less pronounced.
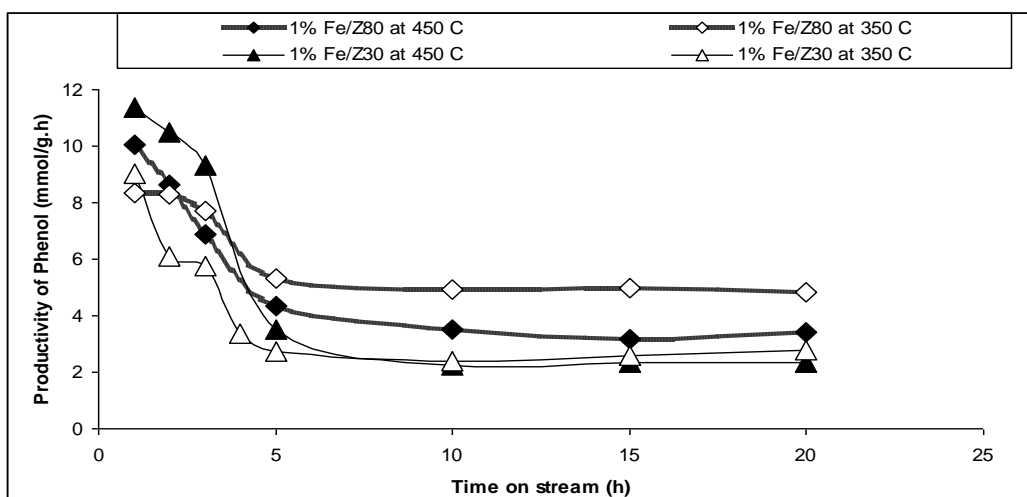
Effect of Si/Al ratio on phenol productivity

At 450°C Fe/Z30 (~11 mmol/g h) shows (see Figure 8) a higher initial reaction rate compared with Fe/Z80 (~9 mmol/g h). However, after 5h the phenol production rate for both samples decreases to ~6 mmol/g h. Composition measurements of the reactor outlet streams at 15h and 20h suggest the Fe/Z30 shows a slightly worse performace in terms of deactivation with phenol production rates around 5 mmol/g h. The 0.1%Fe/Z80 and 0.1%Fe/Z30 have similar reaction rates at 350°C however, the sample 0.1%Fe/Z80 very little deactivation and reaction rate remains stable at around ~6 mmol/g h. The sample 0.1%Fe/Z30 shows deactivation with the rate between 5-20h steady at around ~4 mmol/g h. Thus, for catalyst samples with low iron content (~35mg/g) the Si/Al ratio seems to have an effect on catalyst deactivation. Catalyst samples with high Si/Al ratio showing lower deactivation rates.

Figure 8. Phenol productivities *vs* time on stream using 0.1% Fe/ZSM-5.
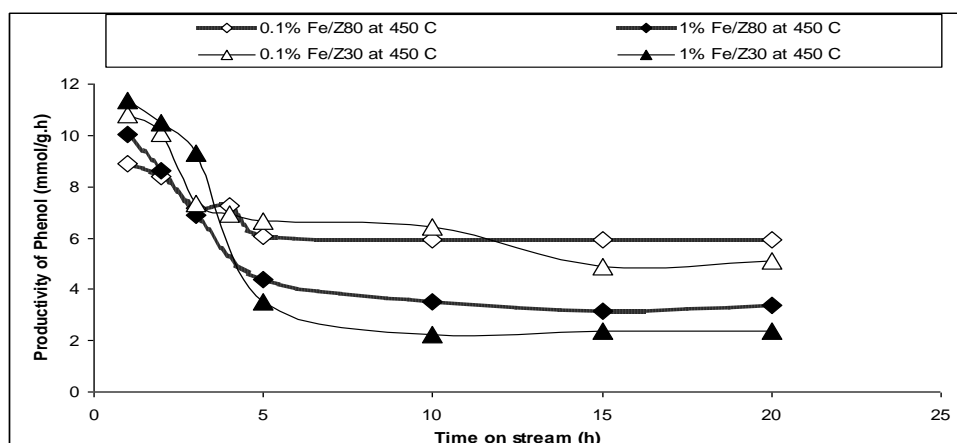
Figure 9. Phenol productivities *vs* time on stream using 1% Fe/ZSM-5.

At 450°C Fe/Z30 (~11.5 mmol/g h) shows (see Figure 9) a higher initial reaction rate compared with Fe/Z80 (~10 mmol/g h). However, after 5h the phenol production rate for both samples decreases Fe/Z30 (~2 mmol/g h) and Fe/Z80 (~4 mmol/g h). The rate of deactivation is considerable more marked in comparison with catalyst samples having lower iron content (see Figure 8). The 1%Fe/Z80 and 1%Fe/Z30 have similar reaction rates at 350°C however, the sample 0.1%Fe/Z80 shows less deactivation and the reaction rate in the stable range (5-20h) is around ~5 mmol/g h. The sample 0.1%Fe/Z30 shows similar deactivation at the lower temperature with reaction rate in the stable range (5-20h) around ~2 mmol/g h. Thus, for catalyst samples with high iron content (~500mg/g) the Si/Al ratio seems to have an effect on catalyst deactivation. Catalyst samples with high Si/Al ratio showing lower deactivation rates.
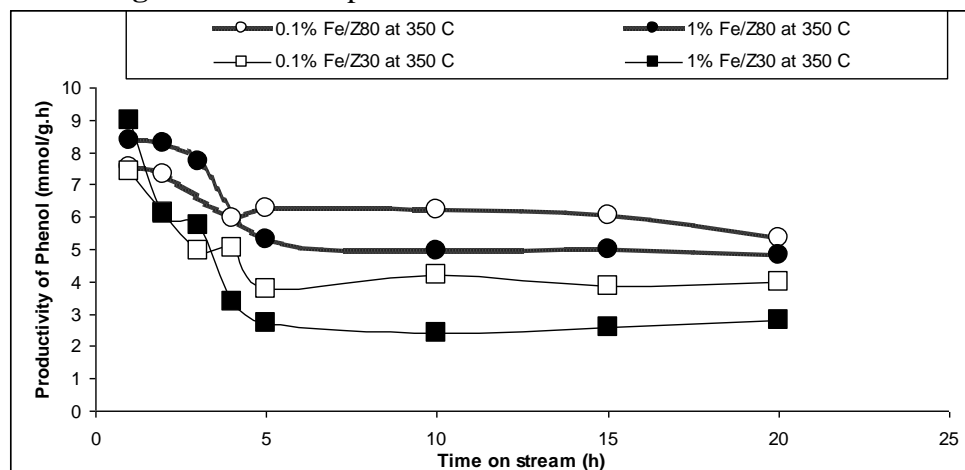
Traces of by products (p-benzoquinone, hydroquinone and catechol) were detected in the outlet stream from the reactor for all catalysts and at all temperatures.

Effect of iron content and temperature on phenol productivity

At 450°C samples with low iron content (irrespective of Si/Al ratio) seems to yield higher phenol reaction rates over the long term (5-20h) and demonstrate greater stability in terms of catalyst resistance to deactivation (see Figure 10). However, samples Z80 seem to show slightly higher reaction rates compared with Z30 post 10h of catalyst operation.

Figure 11. Phenol productivities *vs* time on stream at 350°C.

At 350°C samples with high Si/Al ratio (Z80) seems to yield higher phenol reaction rates (irrespective of iron content) over the long term (5-20h) and demonstrate greater stability in terms of catalyst resistance to deactivation (see Figure 11).

Conclusions

Fe-ZSM5 catalyst samples with different Si/Al ratios and different iron contents have been studied for the one step oxidation of benzene to phenol using N_2O as the oxidant. Catalysts synthesized with high Si/Al ratios and with low iron content seem better suited in terms of long term operation. Catalysts with high amounts of iron showed considerable deactivation. High reaction temperatures (450°C) favour higher reaction rates however, catalysts with high iron content were particularly prone to deactivation at this temperature. The balance between Bronsted acidity and the quantity of active oxygen donor α-sites seem to depend on the Si/Al ratio and the presence of the iron within the catalyst matrix.

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