A hierarchical Fe/ZSM-5 zeolite with superior catalytic performance for benzene hydroxylation to phenol†

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We report the one-step synthesis of a highly active hierarchical Fe/ZSM-5 zeolite catalyst with a strongly improved lifetime in the selective hydroxylation of benzene to phenol with nitrous oxide; compared to the best Fe/ZSM-5 catalyst, the turnover number after 24 h on stream is almost four times higher.

Phenol is an important industrial intermediate for the production of various chemicals such as bisphenol A, phenolic resins, caprolactam, alkylphenols and adipic acid. The cumene hydroperoxide process is the currently used industrial method to produce phenol.† Its environmentally stressing aspects have spurred research to replace this process with more benign approaches such as the direct oxidation of benzene to phenol with nitrous oxide. In Solutia’s AlphOx technology, the nitrous oxide by-product of the manufacture of adipic acid has been considered as a cheap source, because otherwise it has to be treated as waste. The most active and selective catalyst is Fe/ZSM-5 zeolite, but the strong catalyst deactivation due to formation of carbonaceous side-products remains an obstacle in its commercialization. As these deposits can be easily removed by calcination, the process can be operated in a cyclic manner. Yet, the economic viability remains an obstacle in its commercialization.2–11 As these deposits can be easily removed by calcination, the process can be operated in a cyclic manner. Yet, the economic viability is hampered by the relatively strong deactivation of the catalyst. Thus, increasing the catalytic activity or decreasing the rate of deactivation remains a research goal. Steam-calcination of Fe/ZSM-5 substantially improves the catalytic activity and the lifetime before regeneration is required.10 The effect of steaming is understood in terms of an increased number of active Fe sites.4,9,11,12 Hierarchical zeolites are of considerable current interest.13–16 The creation of mesoporosity in ordinary zeolite crystals strongly improves the catalytic performance in reactions that tend to suffer from diffusion limitations. A relevant example is the creation of mesoporosity in HZSM-5 with trace amounts of iron by desilication.17 Such a catalyst has a lower activity than Fe/ZSM-5 materials. Herein, we report that a hierarchical Fe/ZSM-5 catalyst outperforms an optimized steam-calcined Fe/ZSM-5 catalyst: the turnover number to phenol of the hierarchical zeolite is almost four times higher after 24 h on stream. The high accessibility of the small microporous domains renders the zeolite more resistant to deactivation by coke deposits.

In our approach, we added [3-(trimethoxysilyl)propyl]octadecyl(dimethyl)ammonium chloride ((CH₃O)₃SiC₃H₆N(CH₃)₂-C₁₈H₃₇, TPOAC) to the gel to prepare Fe/ZSM-5. The use of amphiphilic organosilanes has recently been explored as a straightforward method to prepare HZSM-5 zeolite with a high degree of mesoporosity.18 This strategy is based on the covalent interaction of a long-chain ammonium surfactant molecule with the growing zeolite crystal surface. The linkage is brought about by a hydrolysable methoxysilyl moiety in the amphiphilic surfactant. In their acidic form, these mesoporous zeolites exhibit improved performance in a number of demanding reactions.19 The active sites for benzene oxidation with nitrous oxide, however, are highly dispersed Fe⁺⁺ centers. These ions are formed upon autoreduction of isolated or at least very dispersed extra-framework ferric ions in the zeolite micropores.2,11,20,21 The desired initial dispersion is preferably obtained by isolating the Fe³⁺ ions in the zeolite framework during hydrothermal synthesis.22 Thus Fe³⁺ was added as the nitrate to a gel to prepare hierarchical ZSM-5 with the final molar composition Al₂O₃/Fe₂O₃/Na₂O/SiO₂/TPABr/H₂O/TPAOAC = 1.2/0.26/40.95/10.26/9000/5. The gel was autoclaved at 150 °C for 4 days (mesoFe/ZSM-5-as). We compared direct calcination in air at 350 °C (mesoFe/ZSM-5) to the alternative procedure which involved the removal of part of the mesoporogen in mesoFe/ZSM-5 by extraction with methanol in a Soxhlet apparatus prior to calcination (mesoFe/ZSM-5-E). The final activation step involved steam calcination at 700 °C following established methods (mesoFe/ZSM-5-S and mesoFe/ZSM-5-ES).9 A reference Fe/ZSM-5 catalyst was prepared according to a standard recipe (Fe/ZSM-5-S).9 The crystallinity of calcined and steamed mesoFe/ZSM-5 zeolites is evident from the vibrational band at 550 cm⁻¹ in their infrared spectra, which is due to the double five-ring vibration of ZSM-5, and the XRD patterns (ESI†). The crystallinity of the hierarchical zeolites estimated by IR spectroscopy is considerably higher (>90%) than that estimated by XRD (50–60%).

Fig. 1 shows the phenol reaction rates of the steamed catalysts. The initial reaction rate of mesoFe/ZSM-5-ES is substantially higher than that of conventional steam-calcined Fe/ZSM-5. Clearly, deactivation of mesoFe/ZSM-5-ES is much lower compared to Fe/ZSM-5-S. As a result, the reaction rate of the hierarchical zeolite is almost four times higher.

† Electronic supplementary information (ESI) available: Experimental details, UV-Vis, XRD, IR, SEM, active site titration, spent catalyst analysis, reaction data. See 10.1039/b917038c
higher than that of Fe/ZSM-5-S after a reaction time of 5 h. This ratio has increased to 24 h on stream. The turnover number (TON) after 24 h on stream is 9.4 g_{\text{phenol}}/g_{\text{zeolite}} for mesoFe/ZSM-5-ES compared to 2.6 g_{\text{phenol}}/g_{\text{zeolite}} for Fe/ZSM-5-S. The TON of an ordered mesoporous Fe/Al-SBA-15,22 which lacks atomic ordering in its aluminosilica network, is only 0.1 g_{\text{phenol}}/g_{\text{zeolite}}.

Fig. 2 shows the N2 sorption isotherms of Fe/ZSM-5-S and mesoFe/ZSM-5-ES. For comparative purposes, the latter isotherm is shifted upwards.

Initially, we hypothesized that the higher catalytic performance of the hierarchical zeolite is due to improved mass transfer. However, we found that the initial intrinsic hydroxylation reaction rates of the various zeolite catalysts are very similar. To this end, we determined the active iron site densities, because only a small part of the iron ions in these catalysts is typically active in benzene hydroxylation.2,4,11,24 Active Fe2+ sites can be titrated by stoichiometric N2O decomposition at moderate temperatures.2,11,25 Titration was done by determining the amount of evolved nitrogen following a step change of the flow from pure He to a gas mixture containing N2O in He at 250 °C. All catalysts contain Fe2+ sites capable of decomposing N2O (Table 1). There are small but significant differences in the active site densities between the catalysts. Steam calcination of mesoFe/ZSM-5-E strongly improves the number of active sites. The beneficial effect of

![Diagram](image-url)

**Fig. 1** Reaction rate of phenol as a function of the time on stream for (△) mesoFe/ZSM-5-ES, (●) mesoFe/ZSM-5-S, and (■) Fe/ZSM-5-S (T = 350 °C, GHSV 30 000 h⁻¹, 1 vol% C6H6 and 4 vol% N2O in He).

**Fig. 2** N2 sorption isotherms of (■) Fe/ZSM-5-S and (△) mesoFe/ZSM-5-ES. For comparative purposes, the latter isotherm is shifted upwards.

**Table 1** Textural and catalytic properties of SBA-15 and zeolite supported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fe (wt%)</th>
<th>Al (wt%)</th>
<th>S_BET (m²/g)</th>
<th>S_{micro pore} (m²/g)</th>
<th>V_{micro pore} (cm³/g)</th>
<th>R_{phenol} (mmol g⁻¹ h⁻¹)</th>
<th>N_a (mmol g⁻¹)</th>
<th>R_{intrinsic} (mmol g⁻¹ h⁻¹)</th>
<th>TON</th>
<th>Coke (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesoFe/ZSM-5-E</td>
<td>1.14</td>
<td>0.56</td>
<td>473</td>
<td>267</td>
<td>0.12</td>
<td>0.30</td>
<td>4.8</td>
<td>2.5 x 10⁻²</td>
<td>192</td>
<td>2.5</td>
</tr>
<tr>
<td>mesoFe/ZSM-5-ES</td>
<td>1.14</td>
<td>0.56</td>
<td>408</td>
<td>161</td>
<td>0.08</td>
<td>0.30</td>
<td>12.0</td>
<td>6.0 x 10⁻²</td>
<td>200</td>
<td>9.4</td>
</tr>
<tr>
<td>mesoFe/ZSM-5-S</td>
<td>1.14</td>
<td>0.56</td>
<td>310</td>
<td>148</td>
<td>0.07</td>
<td>0.19</td>
<td>8.9</td>
<td>4.1 x 10⁻²</td>
<td>217</td>
<td>5.6</td>
</tr>
<tr>
<td>Fe/ZSM-5-S</td>
<td>0.99</td>
<td>0.49</td>
<td>401</td>
<td>262</td>
<td>0.12</td>
<td>0.10</td>
<td>8.4</td>
<td>4.1 x 10⁻²</td>
<td>205</td>
<td>2.6</td>
</tr>
<tr>
<td>Fe/Al-SBA-15</td>
<td>0.21</td>
<td>3.27</td>
<td>780</td>
<td>25</td>
<td>0.01</td>
<td>1.28</td>
<td>0.3</td>
<td>0.9 x 10⁻³</td>
<td>333</td>
<td>0.1</td>
</tr>
</tbody>
</table>

a Rate of phenol formation after 5 min. b Number of active sites determined by N₂O decomposition at 350 °C. c Intrinsic rate of phenol formation after 5 min. d Turnover number during 24 h on stream. e Coke content after 24 h on stream. f Not determined. g From ref. 22.
Intrinsic 5-ES is slightly higher than in Fe/ZSM-5-S. Importantly, the dispersion of Fe (77% of framework Fe as compared to 92% for Fe/ZSM-5-S) is formed in the presence of TPOAC despite the lower initial zeolite crystals. The coke formed during benzene hydroxylation is caused by the deposition of carbonaceous materials in the intersections of the straight and zigzag channels and does not contain large cavities, heavy products become trapped at the inner micropore space, even if part of it becomes blocked by coke deposits. Finally, we confirmed that the high activity and stability of mesoFe/ZSM-5-ES can be regenerated by simple calcination of the spent catalyst ($R_{\text{phenol}} = 12.1 \text{ mmol g}^{-1} \text{ h}^{-1}$ after regeneration) which makes this new material more suitable for the envisioned industrial process.

In summary, a hierarchical Fe/ZSM-5 zeolite catalyst has been developed with a strongly improved performance in benzene hydroxylation to phenol with nitrous oxide. The integration of very small microporous domains into a highly accessible mesoporous matrix alleviates the detrimental effects of pore blocking by carbonaceous deposits.

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Notes and references