

Narrative Progress Report for Shantz ACS PRF ND award 57697-ND5

1. PRF# 57697-ND5
2. Project Title: Cerium Oxide Clusters and Particles as Catalysts for the Oxidation of Benzene to Phenol
3. PI: Daniel Shantz, Tulane University
4. No Co-PI

Research Impact:

This project has had four major thrusts over the current reporting cycle. The first was investigating the reactivity of cerium oxide nanoparticles of varying morphology for the direct oxidation of benzene to phenol using hydrogen peroxide as an oxidant. This route proved unsuccessful unfortunately, as the cerium oxide non-selectively and very rapidly (< 15 minutes) decomposed the hydrogen peroxide, leading to the inability to activate benzene and insert oxygen into the benzene. This was determined in the first six months of the project (we had begun making the catalysts and due to internal delays in setting up the award had many catalysts in hand when the award ‘started’). So while we discovered an excellent hydrogen peroxide decomposition catalyst, it was not a good benzene oxidation catalyst.

With this information in hand we then attempt to modulated the peroxide decomposition rate of the ceria nanoparticles by doping them with a metal such as Au, Cu, and Co (second thrust). This unfortunately did not improve the reactivity of the material. It did lower the peroxide decomposition rate, but did nothing to enable the oxidation of benzene. We have also explored supporting ceria on a variety of supports such as silica and aluminum. Again, no reactivity was observed. The third thrust was to attempt to disperse very small ceria clusters and cerium atoms in an oxide matrix such as a zeolite or mesoporous solid. This unfortunately was also unsuccessful.

The last thrust was stumbled upon by my student Meysam. He was interested in iron containing zeolites for a project he had worked on prior to this grant’s start. When he took those materials he found very high benzene conversion with very high selectivity to phenol (Figure 1). His

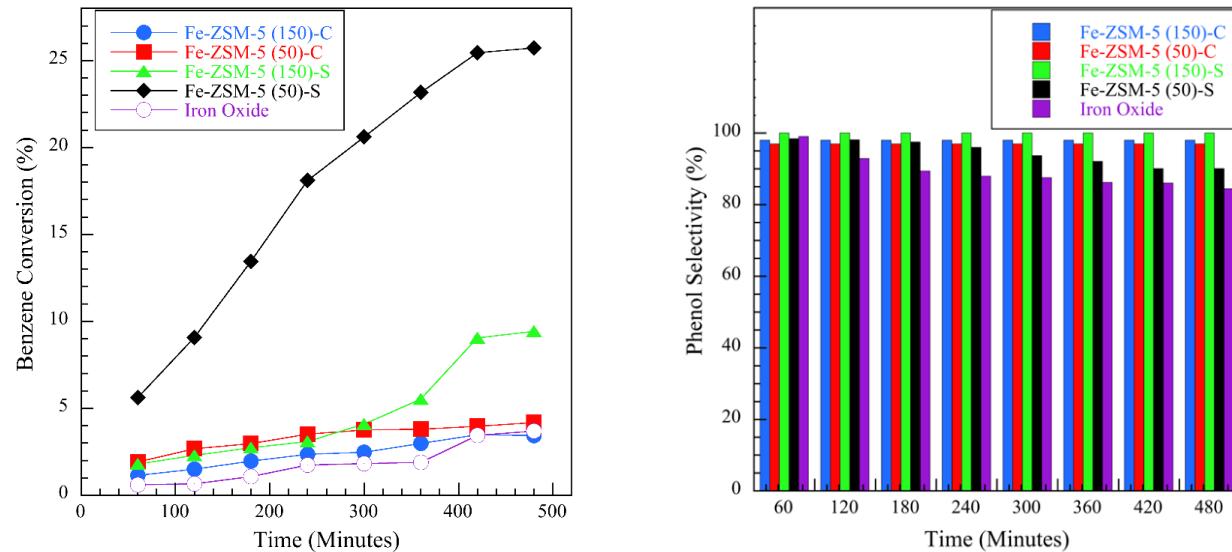


Figure 1. Benzene conversion/phenol selectivity versus time over calcined Fe-ZSM-5 samples and α -Fe₂O₃ particles at 333 K

hierarchically ordered Fe-MFI zeolites are more active than any other metal containing zeolite reported to date. His yield of 20% phenol is superior to nearly all literature catalysts (Table 1). These materials also are very stable. This work is currently under peer review.

| Catalyst | Solvent | T (K) | t (h) | X (%) | Y Phenol (%) | TON |
|--|---------------------|------------|----------|--------------|--------------|---------------|
| TS-1 | Acetonitrile | 333 | 3 | 1.80 | <1.44 | 13.53 |
| TS-PQ™ | Water | 343 | 3 | 19.40 | - | 30.00 |
| TS-1B | Sulfolane | 373 | 1 | 8.60 | 8.08 | 14.66 |
| TS-1A | Methanol/Sulfolane | 353 | 2 | 14.00 | 13.00 | 17.88 |
| TS-1 (50) | Acetonitrile | 333 | 4 | 1.10 | 0.69 | 3.77 |
| TS-1 (150) | Acetonitrile | 333 | 4 | 0.85 | 0.66 | 8.64 |
| [Fe,Al]-MFI | Acetonitrile | 333 | 3 | 2.80 | >2.74 | 34.95 |
| Fe/SBA-16 | Acetonitrile | 338 | 8 | 12.10 | 11.66 | 7.61 |
| Fe-SBA-15 | Acetonitrile | 333 | 8 | 10.67 | 9.39 | 39.31 |
| AC-Fe30 | Acetonitrile | 303 | 7 | 19.60 | 17.50 | 14.63 |
| Fe ₃ O ₄ /CMK-3 | Acetonitrile | 333 | 4 | 18.00 | 16.56 | 34.80 |
| Fe/GO | Acetic Acid | 338 | 3 | 15.90 | 14.96 | 22.60 |
| Fe/MWCNTs | Acetonitrile | 333 | 2.5 | 10.80 | 10.31 | 17.04 |
| α -Fe ₂ O ₃ | Acetonitrile | 333 | 8 | 3.70 | 3.13 | 0.33 |
| Fe(NO ₃) ₃ .9H ₂ O | Acetonitrile | 333 | 8 | 8.46 | 7.34 | 3.85 |
| Fe-ZSM-5 (150)-C | Acetonitrile | 333 | 8 | 3.48 | 3.41 | 50.10 |
| Fe-ZSM-5 (50)-C | Acetonitrile | 333 | 8 | 4.18 | 4.05 | 17.34 |
| Fe-ZSM-5 (150)-S | Acetonitrile | 333 | 8 | 9.50 | 9.50 | 105.63 |
| Fe-ZSM-5 (50)-S | Acetonitrile | 333 | 8 | 25.50 | 22.95 | 81.74 |

Table 1. Comparison of catalytic performance of different iron/titanium based materials for benzene hydroxylation to phenol using H₂O₂ as the oxidant at mild conditions. X is the benzene conversion except for TS-PQ™, which is H₂O₂ conversion. Turn over number was calculated as follows: TON = $\frac{\text{Moles of desired products formed}}{\text{Moles of Fe or Ti}}$. Rows in bold red are samples produced in this work.

Given the success of using these iron containing materials for benzene to phenol, ongoing work is exploring if we can increase the phenol yield further by, for instance, continually adding hydrogen peroxide. The reaction is currently ran in batch mode, and the peroxide conversion is higher than the phenol production, i.e. not all peroxide leads to benzene oxidation. We are also investigating how moving to a flow system from a batch system changes our findings.

Given the success of using the iron zeolites for benzene to phenol, we are now exploring them for the direct oxidation of methane to methanol. This work is preliminary and ongoing.

Impact on the PI's Career

The main impact this work (and support) has had on the PI is to allow him to initiate work in the oxidation catalysis space. The best catalysts discovered so far are very encouraging. The PI plans to leverage this work to further his efforts in the oxidation catalysis space to explore the direct oxidation of methane to methanol, a topic of great interest in the U.S. due to the abundance of shale gas. I am also thinking about additional ways to leverage this work, which may involve industrial partners funding future efforts in the benzene to phenol space.

Impact on the students supported

The students involved in this work will obtain high visibility due to the importance of the problem and the nature of the journal in which the work will be published. Both students who have been supported on this award during the current cycle are interested in academic careers, and this program should align them well with that aim. As one example, INE.OS has contacted me about our work given their interest in phenol production technology