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OBJECTIVES

The overall objective of this research project is to obtain the reaction engineering information required to evaluate the utility of catalytic supercritical water oxidation (SCWO) for treating wastes arising from coal conversion processes. Our more specific objectives for this first phase of the project were:

1. to recruit and train a graduate student to work on this project
2. to construct a reactor system for the experimental studies
3. to initiate catalytic SCWO experiments and identify an active catalyst.

Each of these three objectives has been met.

SUMMARY OF TECHNICAL PROGRESS

Introduction

The literature (1-8) revealed that both CuO and MnO₂ are effective catalysts for the oxidation of organics (including phenol) in aqueous streams. Recently, these materials have also shown promise in catalytic supercritical water oxidation (9, 10). Accordingly, our initial experiments have employed CuO and MnO₂ catalysts that are commercially available. The catalyst we used in these initial studies, CARLITE 150 from Carus Chemical Company, has been commercially used in treating volatile organic compounds generated in various chemical processes. It contains MnO₂ and CuO supported on Al₂O₃. The commercial catalyst pellets were ground to powders and separated by size before use. We used phenol as the first model pollutant to study because it is ubiquitous in wastewaters and there is a large data base for non-catalytic SCWO with which we can contrast results from catalytic SCWO.

Experimental Section

Phenol oxidation experiments were performed at 380 °C and 248 atm in isothermal, tubular reactors that contained carefully weighed amounts of catalyst particles (125 ~ 250 μm in diameter). Porous Hastelloy disks are placed at the ends of the reactor to hold the catalyst inside. Aqueous feed streams of phenol and oxidant are preheated separately to the reaction temperature in two 1/16-in. (1.6-mm) OD feed lines before being mixed in a Hastelloy C-276 cross, which marks the beginning of the reactor. The initial phenol concentration ranged from 4.9 × 10⁻⁴ to 1.6 × 10⁻³ M and the oxygen concentrations were between 1.5 × 10⁻² to 6.3 × 10⁻² M. We initially used reactors constructed of 1/4-in. (6.4-mm) OD Hastelloy C-276 tubing with lengths between 4.4 cm to 15 cm. Later, we used smaller reactors, which comprised two 1/4-in. port connectors and one union, all made of stainless steel by Swagelok. The catalyst was placed inside the union and the porous disks were placed at both ends. In all cases, the reactor assembly was housed in a temperature-controlled fluidized sand bath that maintains isothermality to within 1 °C. Upon leaving the heated zone of the sand bath, the reactor effluent was cooled and then depressurized and separated into vapor and liquid phases. Unreacted phenol in the reactor effluent is quantified to within 2% using reversed-phase, isocratic, high-performance liquid chromatography (HPLC). We used a C18 column, a mobile phase of acetonitrile and water (28:72 by volume) and UV detection at 210 nm. Quantification of CO₂ and CO
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is accomplished with an on-line gas chromatograph with thermal conductivity
detector (GC-TCD).

Results and Discussion

Our initial experiments employed the tubular reactors fully packed with
catalyst. This arrangement consistently achieved complete phenol oxidation to CO₂,
even when the reactor length (and catalyst bed depth) was reduced to our
experimentally achievable lower limit of ~ 4 cm. In terms of the catalyst contact
time (defined as ratio of catalyst mass to mass flow rate through the reactor), we
achieved complete oxidation in the range of 3 to 15 seconds.

Our desire is to obtain kinetic data at lower phenol conversions, so we used
varying (but much smaller) amounts of catalyst (0.0150 g to 0.0890 g) inside the
tubular reactor. The volume of this reactor is only 1.2 ml. The bulk volume of
catalyst used in these experiments (up to 0.1 ml) was still just a small fraction of the
total reactor volume, however. By reducing the amount of catalyst in the reactor as
described, phenol conversions of 33% - 89% and CO₂ yields of 12% - 66% were
achieved. These conversions and CO₂ yields are significantly higher than those that
would be achieved by the homogeneous, non-catalytic SCWO of phenol under
identical conditions. We observed, however, that the phenol conversion and CO₂
yield did not exhibit smooth trends as the amount of catalyst used was varied. This
behavior is likely due to the catalyst being pushed to the end of the reactor by the
flowing fluid and the plug-flow pattern being destroyed.

To test this hypothesis, we reconstructed the reactor (using Swagelok port
connectors and a union) and placed the catalyst in the middle portion of the reactor.
Results from this configuration were a much smoother function of the contact time,
and we conclude that these experimental conditions are not accompanied by non-
ideal flow patterns.

Table I: Summary of Phenol Oxidation Experiments (47 mg catalyst, 380°C, 248 atm)

<table>
<thead>
<tr>
<th>Run</th>
<th>Contact Time (s)</th>
<th>Residence Time (s)</th>
<th>[PhOH] mM</th>
<th>[O2] mM</th>
<th>Non-Cat Conv., %</th>
<th>Catalytic Conv., %</th>
<th>CO2 Yield, %</th>
<th>CO Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.51</td>
<td>5.86</td>
<td>0.93</td>
<td>44.02</td>
<td>19.28</td>
<td>97.01</td>
<td>80.45</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>0.35</td>
<td>4.02</td>
<td>1.25</td>
<td>30.19</td>
<td>10.91</td>
<td>87.64</td>
<td>75.51</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>2.85</td>
<td>1.46</td>
<td>21.35</td>
<td>6.47</td>
<td>83.28</td>
<td>43.30</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>2.92</td>
<td>0.95</td>
<td>43.28</td>
<td>9.92</td>
<td>85.25</td>
<td>66.16</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>0.19</td>
<td>2.21</td>
<td>1.19</td>
<td>32.86</td>
<td>6.44</td>
<td>74.04</td>
<td>57.35</td>
<td>0.47</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>1.93</td>
<td>0.97</td>
<td>42.34</td>
<td>6.56</td>
<td>74.59</td>
<td>46.96</td>
<td>0.32</td>
</tr>
<tr>
<td>7</td>
<td>0.41</td>
<td>4.76</td>
<td>0.93</td>
<td>43.85</td>
<td>15.87</td>
<td>91.95</td>
<td>79.72</td>
<td>0.32</td>
</tr>
<tr>
<td>8</td>
<td>0.26</td>
<td>2.97</td>
<td>1.32</td>
<td>27.39</td>
<td>7.73</td>
<td>79.63</td>
<td>63.73</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Tables I and II summarize two series of experiments using 0.0470 g and 0.1410
g of catalyst, respectively. Phenol conversions range from 74% at the contact time of
less than 0.2 second to 100% at over 1 second. By contrast, the phenol conversions
due to homogeneous oxidation were calculated to be between 4% to 29%. These
calculations were done by using a rate law in the literature for non-catalytic SCWO.
of phenol (11). The effect of the catalyst is even more impressive when considering that the bulk volume of catalyst (0.06 - 0.16 ml) was less than 14% of the total reactor volume (1.2 ml). Thus, the heterogeneous SCWO occurs only in a small portion of the reactor while the homogeneous SCWO occurs in the entire reactor.

Table II: Summary of Phenol Oxidation Experiments (141 mg cat, 380°C, 248 atm)

<table>
<thead>
<tr>
<th>Run</th>
<th>Contact Time, s</th>
<th>Residence Time, s</th>
<th>[PhOH] mM</th>
<th>[O2] mM</th>
<th>Non-Cat Conv., %</th>
<th>Catalytic Conv., %</th>
<th>CO2 Yield, %</th>
<th>CO Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.79</td>
<td>3.02</td>
<td>0.68</td>
<td>54.71</td>
<td>12.01</td>
<td>100.00</td>
<td>81.35</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.58</td>
<td>2.22</td>
<td>1.02</td>
<td>40.27</td>
<td>7.30</td>
<td>99.50</td>
<td>78.37</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>1.81</td>
<td>6.95</td>
<td>0.49</td>
<td>63.03</td>
<td>28.69</td>
<td>100.00</td>
<td>108.28</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>1.24</td>
<td>4.78</td>
<td>0.94</td>
<td>43.35</td>
<td>15.83</td>
<td>100.00</td>
<td>94.89</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.78</td>
<td>2.99</td>
<td>1.32</td>
<td>27.09</td>
<td>7.73</td>
<td>99.11</td>
<td>85.16</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>1.06</td>
<td>4.06</td>
<td>0.56</td>
<td>59.88</td>
<td>17.02</td>
<td>100.00</td>
<td>104.03</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>0.76</td>
<td>2.94</td>
<td>0.95</td>
<td>43.88</td>
<td>10.05</td>
<td>97.28</td>
<td>77.98</td>
<td>0.67</td>
</tr>
<tr>
<td>8</td>
<td>0.61</td>
<td>2.33</td>
<td>1.15</td>
<td>34.80</td>
<td>6.99</td>
<td>94.54</td>
<td>70.99</td>
<td>0.72</td>
</tr>
<tr>
<td>9</td>
<td>0.58</td>
<td>2.21</td>
<td>1.62</td>
<td>14.71</td>
<td>4.15</td>
<td>94.16</td>
<td>50.87</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The figure below illustrates the effect of contact time on the phenol conversion and CO2 yield. Phenol conversions quickly approach 100%, and no phenol was detected from the reactor effluent when the residence time exceeded 1 second. The complete oxidation of organic carbon to CO2 is a little slower, but the trend is similar. Perhaps the biggest improvement of catalytic SCWO over non-catalytic SCWO is the high selectivity to CO2. The CO2 yield is almost always close to the phenol conversion. It is 80% when the phenol conversion first approaches 100%. At slightly longer contact times, it eventually reaches 100%. In our previous study of homogeneous SCWO of phenol, on the other hand, we found that the phenol conversion could approach 100% by operating at very long residence times,
but the CO₂ yield only approached 50-60% (12). Such incomplete oxidation is necessarily accompanied by the formation of complex intermediate products from dimerization, ring-opening and partial oxidation (13, 14). Suppressing the formation of these products of incomplete oxidation is one of the major reasons that prompted us to study catalytic SCWO. Although a complete analysis of the intermediate byproducts from catalytic SCWO needs to be done (and is under way) before a conclusion can be made, the high CO₂ yields obtained in this study does suggest that the yields of such products are greatly reduced. Another sign of more complete oxidation is the yield of CO which was always less than 1% compared to up to 5% in homogeneous SCWO studies. It is highly encouraging that catalytic SCWO not only accelerates the disappearance of phenol but also promotes complete oxidation, which appears to be achieved at contact times of only a few seconds when more than 200% excess O₂ is used.

The experiments described above were conducted using fresh catalyst. Table III lists a series of data collected from a catalyst aged for two days under SCW conditions.

Table III: Summary of Phenol Oxidation Experiments under same conditions as, but two days after, those in Table II

<table>
<thead>
<tr>
<th>Run</th>
<th>Contact Time, s</th>
<th>Residence Time, s</th>
<th>[PhOH] mM</th>
<th>[O₂] mM</th>
<th>Non-Cat Conv., %</th>
<th>Catalytic Conv., %</th>
<th>CO₂ Yield, %</th>
<th>CO Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.68</td>
<td>6.47</td>
<td>0.92</td>
<td>45.03</td>
<td>21.32</td>
<td>97.84</td>
<td>85.40</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>1.32</td>
<td>5.05</td>
<td>1.14</td>
<td>35.16</td>
<td>14.72</td>
<td>95.36</td>
<td>78.78</td>
<td>0.91</td>
</tr>
<tr>
<td>3</td>
<td>1.06</td>
<td>4.07</td>
<td>1.30</td>
<td>28.32</td>
<td>10.63</td>
<td>92.03</td>
<td>71.26</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>1.21</td>
<td>4.64</td>
<td>0.93</td>
<td>44.43</td>
<td>15.60</td>
<td>95.09</td>
<td>77.64</td>
<td>1.09</td>
</tr>
<tr>
<td>5</td>
<td>0.77</td>
<td>2.94</td>
<td>1.30</td>
<td>28.20</td>
<td>7.78</td>
<td>88.98</td>
<td>67.09</td>
<td>0.92</td>
</tr>
<tr>
<td>6</td>
<td>1.67</td>
<td>6.41</td>
<td>0.93</td>
<td>20.74</td>
<td>14.79</td>
<td>94.45</td>
<td>74.63</td>
<td>0.88</td>
</tr>
<tr>
<td>7</td>
<td>1.31</td>
<td>5.03</td>
<td>1.15</td>
<td>16.28</td>
<td>10.18</td>
<td>89.87</td>
<td>64.80</td>
<td>0.86</td>
</tr>
</tbody>
</table>

The phenol conversions obtained from this aged catalyst were about 5 - 10% lower while the CO₂ yields decreased by ~ 20% relative to their values in Table II. Whether this effect is due to the aging of catalyst (which is likely since the catalyst support material, Al₂O₃, could crystallize under SCW condition) or simply because it takes a certain amount of time on stream for the catalytic oxidation to be stabilized is not clear at this stage, and is under investigation. Also noteworthy from Table III is that data points #6 and #7 were obtained from experiments at conditions identical to those used to obtain points #1 and #2 except the O₂ concentration was reduced by half. The phenol conversions decreased by ~ 5% while the CO₂ yields decreased by ~ 15%, suggesting that the O₂ concentration more strongly influences the CO₂ formation kinetics than the phenol disappearance kinetics. Qualitatively, this is similar to the kinetics of CO₂ formation in homogeneous SCWO. A detailed study of the kinetics of both process is under way.

Conclusion

Within the phenol concentration range from 4.9 × 10⁻⁴ to 1.6 × 10⁻³ M and oxygen concentrations in 30% ~ 1740% excess, we found that the use of the
commercial catalyst improved SCWO of phenol dramatically in terms of both rate and selectivity. The rates of the phenol destruction and CO$_2$ formation seem to improve by more than an order of magnitude. The O$_2$ concentration appears to be a factor in the kinetics of both processes, but a more important factor for CO$_2$ formation. Complete oxidation to CO$_2$ has been achieved in several seconds when oxygen is in large excess amount. These results hint at the great potential that catalytic SCWO might have for completely oxidizing phenol at relatively mild conditions, perhaps at temperatures just above Tc (374 °C) instead of over 600 °C that is commercially proposed to treat organic waste like phenol by non-catalytic SCWO.

**Future Plans**

Since the commercial catalyst we used showed promising results, experiments will be conducted on this catalyst, with systematic variations in phenol concentration, O$_2$ excess amount, temperature, pressure and catalyst amount, in order to establish global rate laws to model the catalytic SCWO. Before getting into this detailed kinetics study, we will first verify that the results we obtained so far are not influenced by either internal or external mass-transfer limitations. Kinetic data at lower phenol conversion will be pursued, and byproducts in the liquid phase will be analyzed from the reactor effluent to probe the effect of catalyst on dimerization, partial oxidation, and ring-opening reaction pathways. The stability and durability of the catalyst will also be studied, by investigating its aging effect on activities and selectivity, and by evaluating the catalyst itself after the kinetic study. Finally, oxidation using other catalysts (especially containing MnO$_2$ and CuO) will also be investigated.

**REFERENCES**