THE EFFECTS OF NANOPARTICLE IRON OXIDE ON CO AND NO REMOVAL IN BIOMASS PYROLYSIS AND OXIDATION PROCESSES

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Introduction

Nanoparticle iron oxide such as NANOCAT® Superfine Fe$_3$O$_4$ (referred as NANOCAT® hereafter) by Mach I, Inc. was evaluated as a potential catalyst for Direct Coal Liquefaction (DCL) process shortly after it became available. Recently, it was found that the material, which has an average particle size of 3 nm, was an efficient CO catalyst with a performance far better than other supported or unsupported iron oxide. It is also known that the reduced form of Fe$_3$O$_4$ such as Fe$_2$O$_3$ is the effective catalytic component for CO + NO reaction. Therefore, NANOCAT® could potentially be used as a catalyst for the simultaneous CO and NO removal in biomass pyrolysis and combustion, for example, in cigarette.

The kinetics of NANOCAT® as a CO catalyst in the well-controlled gaseous environments of CO and O$_2$ has been presented elsewhere. However, the performance of a CO/NO catalyst in a clean, contaminant-free gaseous environment is not necessarily transferable to the application of biomass pyrolysis and combustion since a lot of other pyrolytic products could potentially deactivate the catalyst. In this study, biomass was pre-mixed with NANOCAT® prior to pyrolysis and oxidation. The mixed NANOCAT® went through the pyrolysis and the oxidation processes with biomass and its effect on CO and NO removal was then evaluated. The experimental results on biomass were compared to those obtained in the controlled gaseous environment and the possible difference in the catalytic mechanism under two different conditions was discussed.

Experimental

Materials. The NANOCAT® sample was purchased from MACH I, Inc. (King of Prussia, PA.). The sample was a free flow, brownish color powder with a bulk density of only 0.05 g/cm$^3$. The average particle size was 3 nm and the BET surface area was 250 m$^2$/g, according to the manufacturer. The biomass sample used in the experiment was a mixture of tobacco powders including Bright, Burley, and Oriental. Sample also contained 7% moisture. The inlet gases to the flow tube were controlled by a Hastings digital flow meter. The effluents first passed through an ultra fine fiber glass filter pad to collect the room temperature condensables. The gases were then analyzed by an online NGA2000-MLT multi-gas analyzer from Rosemount Analytical. The analyzer used non-dispersive near infrared detectors for CO, NO and CO$_2$, and a paramagnetic detector for oxygen. The rate of data acquisition was one measurement for all gases per second.

A two-step experiment of pyrolysis and oxidation was carried out for both pure biomass and biomass mixed with NANOCAT®. In the first step, sample was heated at about 12 °C/min. heating rate to 350 °C with a hold time of 20 minutes under 500 mL/min. flow of helium. After the sample was completely cooled down to the ambient temperature, the second step, the oxidation of the freshly formed char was performed. In this step, the inlet gas containing 21% O$_2$ was flown at 500 mL/min., and the temperature was raised from ambient to 750 °C at about 12 °C/min. heating rate. CO, NO, and CO$_2$ production in both steps, and O$_2$ consumption in the second step were measured. The condensate collected in the pyrolysis step was also gravimetrically measured.

The catalytic performance of NANOCAT® for CO + O$_2$ and CO + NO reactions in the well-controlled gaseous environments were evaluated in the same setup but with a narrower quartz tube (I.D.: 0.8 cm). The total gas flow rate was fixed at 1000 mL/min. and the NANOCAT® used in each test was 50 mg.

Results and Discussion

Under the well-controlled gaseous condition, NANOCAT® was an efficient catalyst for the 2CO + O$_2$ = 2CO$_2$ reaction, as shown in Figure 1. The performance of NANOCAT® was significantly better compared to the other forms of iron oxide such as α-Fe$_2$O$_3$. The onset temperature was at least 100 °C lower and the CO conversion efficiency was almost ten times higher. The dramatic improvement was attributed to the small particle size and the existence of the FeOOH phase in NANOCAT®. In the absence of O$_2$, NANOCAT® was reduced by CO to form FeO$_x$, FeO, and Fe, which were catalysts for the 2CO + 2NO = 2CO$_2$ + N$_2$ reaction, also shown in Figure 1.

![Figure 1. Flow tube test of NANOCAT® as the catalyst for (a) CO + O$_2$ reaction, (b) CO + NO reaction.](image-url)
The pyrolysis and oxidation of mixture of biomass and NANOCAT® constitute a much more difficult chemical environment for CO and NO catalysts to be effective. Many products evolved during the pyrolysis of biomass could potentially deactivate the catalysts. Thus, it is important to investigate the performance of NANOCAT® in an environment controlled by the biomass pyrolysis and oxidation processes. The tests were carried out by mixing biomass and NANOCAT® together and the mixtures then underwent the pyrolysis and the subsequent char oxidation process, as the control biomass sample. The results are shown in Figure 2 and the integrated data are summarized in Table 1. It can be clearly seen that the effects of NANOCAT® on CO, CO₂, and NO evolution during the pyrolysis were minimal. The only notable change was that with NANOCAT®, NO evolved at lower temperature. However, significant changes were observed in the subsequent char oxidation process of the sample with NANOCAT®. CO production was reduced by 67%, from 1.89 to 0.63 mmol, and NO was also reduced by 57%, from 0.060 to 0.026 mmol. Since the CO oxidation is highly exothermic, a bigger temperature rise was observed for the sample by 57%, from 0.060 to 0.026 mmol. This is clearly another possible mechanism to explain the decrease of NO production in the oxidation step of the biomass mixed with NANOCAT®. Additional tests were carried out to verify if the existence of NANOCAT® would promote the NO + char reaction. The experiments were done by simply switching 21% O₂ to 1500 ppm of NO in the oxidation steps. As shown in Figure 3, the onset temperature of NO + char reaction was reduced in the biomass char sample with NANOCAT® and the complete NO removal was achieved at a temperature less than 400°C, which was more than 200°C lower compared to the control sample.

In addition to the CO + NO reaction, NO + char reaction could also contribute to the total removal of NO. It can be clearly seen that the decrease of NO production in the oxidation step of the biomass mixed with NANOCAT®. Additional tests were carried out to verify if the existence of NANOCAT® would promote the NO + char reaction. The experiments were done by simply switching 21% O₂ to 1500 ppm of NO in the oxidation steps. As shown in Figure 3, the onset temperature of NO + char reaction was reduced in the biomass char sample with NANOCAT® and the complete NO removal was achieved at a temperature less than 400°C, which was more than 200°C lower compared to the control sample.

Table 1. Summary of the Pyrolysis and Oxidation Results (mmol)

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>CO₂</th>
<th>NO</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>Control</td>
<td>0.18</td>
<td>1.11</td>
<td>0.049</td>
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<tr>
<td></td>
<td>Test</td>
<td>0.21</td>
<td>1.17</td>
<td>0.047</td>
</tr>
<tr>
<td>Char</td>
<td>Control</td>
<td>1.89</td>
<td>5.93</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>Test</td>
<td>0.63</td>
<td>8.37</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Acknowledgment

The support of Philip Morris USA management on fundamental science research is gratefully acknowledged.

References