Fischer-Tropsch Synthesis over Supported Nano-iron Catalysts
Synthesized by Gas-Expanded Liquid Deposition Technique

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Introduction
In this study, a new catalyst was prepared using pre-synthesized iron oxide nanoparticles that were controllably deposited onto a support using a gas-expanded liquid precipitation technique (GXL). The effectiveness of this novel catalyst system was tested for FTS performance in a fixed bed tubular reactor. A GXL is a mixed solvent composed of a compressible gas like CO₂ or ethane dissolved in an organic solvent. Due to the expansion of the liquid-organic solvent upon gas dissolution, the viscosity, diffusivity and solubility are tunable through simple adjustments in the applied pressure. The lower viscosity, higher mass transfer coefficient, and diminished interfacial properties in the GXL enhance the diffusivity of the iron particles into the catalyst pores. Using the GXL technology, previously synthesized iron oxide nano-particles can be efficiently deposited onto the surface, and inside the pores, of a desired support material via CO₂ pressurization of a mixture of a support material, organic solvent, and dispersed iron oxide particles. This method allows us to generate a supported iron catalyst with a narrow size distribution of iron oxide nano-particles for Fischer Tropsch synthesis. This paper reports on the preparation and optimization of these new nano iron oxide catalysts and their catalytic performance in terms of suitable activity and product selectivity. These nano iron oxide catalysts were compared to conventional catalysts prepared by the incipient wetness method using the same iron oxide loading. In addition, the influence of the type of support material employed, the iron oxide loading amount, as well as the surface areas of the support materials on the FT catalytic performance have been evaluated.

Materials and Methods
Iron oxide nanoparticles coated with oleic acid were synthesized based on a method described previously by Jain et al.[1]. A schematic of the reactor vessel used and the deposition process is shown in Figure 1. A known quantity (8 g) of the powdered oxidic support is first added to the reactor along with the dispersion of oleic acid-coated iron oxide nanoparticles in n-hexane. The impeller is set to a speed of 200 rpm and the reactor is purged of all air using CO₂. The pressure in the reactor is then slowly increased (over a period of one hour) by injecting CO₂ into the reactor until the system pressure reached 700 psi. The reactor is then maintained at this condition for a period of 20 hours to ensure that the n-hexane completely expands and that the system reaches equilibrium. After 20 hours, the impeller is stopped and the particles are allowed to settle for 30 minutes. Then, the gas-expanded hexane is displaced from the reactor into the collection vessel via slowing opening the valve V2. The hexane removal continues until only CO₂ gas escapes the siphon tube outlet and no liquid effluent is observed. The system is then slowly depressurized (using valve V2) until the pressure in the system reaches atmospheric pressure. The catalyst precursor then go through drying and a subsequent calcination process at 375 °C under a flow of air for 4 hours.

Results and Discussion
CO conversions for these four catalysts are shown in Table 1. It is observed that the catalysts prepared by the incipient wetness method demonstrated low CO conversions, specifically 6.56% for the Fe/Al₂O₃ IW and 13.78 % for the Fe/SiO₂ IW catalyst. On the contrary, the catalysts prepared by the gas expanded liquid technique showed different CO conversions with respect to the catalyst support materials used. The difference in the CO conversion can be attributed to the effect of support materials as well as the preparation method used in this study. Bukur and Sivaraj [2] reported that silica supported Fe catalyst were more active than the alumina supported catalysts. The inferior activity of the alumina supported catalyst was ascribed primarily to its lower degree of reduction, along with the nature of iron phases present and their crystallite particle size. Alternatively, Galvis et al. believed that the strong metal-support interaction inhibits the formation of catalytically active iron phase, resulting in low FT activities.[3] In this study, it is very interesting to find that the Fe/SiO₂ GXL catalyst possess a significant higher CO conversion than the other three catalysts. Based on the H₂-TPR results and the discussion above, it is reasonable to attribute this significant increase in CO conversion to the weaker interaction between the iron oxide particles and SiO₂ supporting materials, which has been demonstrated by the H₂-TPR profiles.

Table 1. CO conversion and product selectivity of the iron catalysts prepared by GXL and incipient wetness method (IW), at a condition of 2.0 MPa, 230 °C, and H₂/CO = 1.70

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO conversion (%)</th>
<th>CO₂ selectivity (%)</th>
<th>Hydrocarbon selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₁</td>
</tr>
<tr>
<td>10% Fe/MO-GXL</td>
<td>12.28</td>
<td>6.72</td>
<td>54.07</td>
</tr>
<tr>
<td>10% Fe/SiO₂-GXL</td>
<td>60.64</td>
<td>27.31</td>
<td>33.40</td>
</tr>
<tr>
<td>10% Fe/Al₂O₃-IW</td>
<td>6.56</td>
<td>21.71</td>
<td>49.35</td>
</tr>
<tr>
<td>10% Fe/SiO₂-IW</td>
<td>13.78</td>
<td>19.54</td>
<td>29.42</td>
</tr>
</tbody>
</table>

Significance
The catalysts prepared by the GXL technique employed in this study show weaker interactions between the iron oxide nanoparticles and the support material, offering a new strategy to investigate the effect of metal-support interaction on the activity and selectivity of iron based FT synthesis catalysts.

References