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High Temperature Alkene Oligomerization on Single Site Cobalt Catalysts

By: Ethan Edwards

Abstract:
Global demand for energy is continually increasing and it is vital that researchers discover more efficient and sustainable methods for utilizing scarce resources. Shale gas is a form of natural gas that is trapped within shale formations and has become an increasingly vital source of natural gas for the United States through the development of the hydraulic fracturing extraction process. Heterogeneous, non-acidic catalysts can be used to convert the light alkanes in shale gas to more usable and transportable products. Catalytic shale gas conversion is a two-step process that includes the dehydrogenation of light alkanes to olefins and then the oligomerization of olefins to longer chain products. These two processes are traditionally performed under different reaction temperatures and pressures. However, the two reactions are proposed to be related due to common metal-hydride and metal-alkyl intermediates. Single-site cobalt catalysts (Co^{2+}/SiO_2) are active in propane dehydrogenation, where the olefin selectivity was >95% at 6% conversion. This suggests that Co^{2+} forms the necessary reaction intermediates for oligomerization. This project demonstrates that Co^{2+} can also catalyze olefin oligomerization at high temperatures through dimerization tests. Dimerization tests of pure ethylene resulted in low conversions (~3%) to C4 products, along with the presence of other higher molecular weight hydrocarbons. Tests at higher pressures are expected to form liquid fuel products. This transformation to liquid fuel products will allow shale gas to be compatible with the current United States transportation infrastructure, further making it a viable alternative fuel.

Research Purpose:
Global demand for energy is continually increasing and there is a concentrated effort for scientists and engineers to discover more efficient and sustainable methods for utilizing scarce resources. Shale gas is a form of natural gas that is trapped within shale formations and has become an increasingly vital source of natural gas for the United States through the recent development of the hydraulic fracturing extraction process. As of 2017, shale gas makes up 60% of the U.S. total dry natural gas production as shown in Figure 1.
Figure 1: Monthly U.S. shale gas production continues to increase in the United States. Shale gas, which contains light alkanes including methane, ethane, and propane, is known for having lower overall greenhouse gas emissions than traditional coal resources. It is presently being employed to produce olefins. Olefins, which are most notably ethylene and propylene, are important chemical intermediates that are used in the production of petrochemicals and can be further converted to fuel products via oligomerization. Traditionally, Ni-based catalysts are being used to perform this chemistry, but reaction conditions are limited to low temperatures. Alternatively, high temperature oligomerization catalysts are desirable to couple alkane and olefin conversion into a single step, streamlining the current industrial process. This project aims to implement cobalt single site catalysts (Co^{2+}) in high temperature oligomerization processes, with the ultimate goal of converting alkanes directly to long chain olefins. The scope of this research is limited to understanding only the oligomerization reaction.

Background:

Figure 2: Dehydrogenation and oligomerization processes transform alkanes to high carbon fuel products. Dehydrogenation and oligomerization processes are vital to the processing of light alkanes to liquid fuels and are traditionally two separate processes in an industrial setting. Although reaction conditions of temperature and pressure differ, dehydrogenation (500°C - 750°C and 1 atm) and oligomerization (200°C and 10-15 atm) both feature a coordination insertion mechanism, Figure 2. The olefin monomer coordinates to the vacant coordination site of the metal center. The subsequent formation of the M-R bond by alkylation of a metal hydride then occurs. β-hydride elimination and transfer results in the formation of an M-H site and higher molecular weight products.

Figure 3: The relationship between dehydrogenation and oligomerization is based on the shared mechanism of a metal hydride formation. Currently, there are no known commercial technologies that perform both reactions at high temperatures in a single reactor. If a catalyst performs dehydrogenation, it likely forms the necessary intermediates to perform oligomerization under the same conditions.
Method:
Catalyst development requires an understanding of the structure and chemical reactivity. To better understand this, a single-site cobalt catalyst (Co$^{2+}$/SiO$_2$) was synthesized using strong electrostatic absorption, a standard method where the pH is controlled to charge the support surface and allow for the absorption of Co$^{2+}$ sites to the surface. The catalyst was prepared by first suspending 10 g of Silica in 100 mL of deionized water. The pH of the solution was adjusted to 11 using ammonium hydroxide (NH$_4$OH). Meanwhile, 2.5 g of Co(NH$_3$)$_6$Cl$_3$ was dissolved in 25 mL of deionized water and the pH was adjusted to 11. The two solutions were combined and stirred at room temperature. After stirring, the solution was given approximately five minutes to settle and decanted. The wet powder was vacuum filtered, rinsed three times with deionized water, and dried overnight in a drying oven set to 125°C. The catalyst was then calcined at 300°C for 3 hours with a 1-hour ramp rate. Atomic adsorption spectroscopy of the catalyst revealed that the cobalt loading on silica was 3%.

Figure 4: The method of strong electrostatic adsorption for a single site cobalt catalyst. The oxidation state and coordination geometry were determined by X-Ray Absorption Spectroscopy (XAS) at Argonne National Laboratory to confirm a 4-coordinate single site structure. The oxidation state was also determined to be Co$^{2+}$ as shown in Figure 5.

Results:
Hydrogenation of Propylene

Propylene hydrogenation, \( \text{C}_3\text{H}_6 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 \), was active at a steady state for over an hour. Tests were conducted at 200°C after the catalysts were pretreated at the same temperature. The results are shown in Table 1. \( \text{H}_2 \) and \( \text{N}_2 \) pretreatments were both measured.

Table 1: Initial TORs for Co\(^{2+}\)/SiO\(_2\) after testing in propylene hydrogenation (200°C)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Pretreatment</th>
<th>TOF (1/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>( \text{H}_2 )</td>
<td>1.791</td>
</tr>
<tr>
<td>200</td>
<td>( \text{N}_2 )</td>
<td>0.449</td>
</tr>
</tbody>
</table>

Dehydrogenation of Propane

Dehydrogenation \( (\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2) \) was investigated at 550°C and atmospheric pressure. Results indicate that selectivity is inversely proportional to conversion. Turnover frequency (TOF), which is the rate at which the cobalt catalyst undergoes a catalytic cycle, also increased with temperature. Tests were not completed above 550°C due to confounding reactions that include thermal cracking, isomerization, and catalyst coking.

Table 2: Conversion and selectivity data for propane dehydrogenation (1 atm, 550°C)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>X(%)</th>
<th>S(%)</th>
<th>Initial TOF (1/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>1</td>
<td>99</td>
<td>2x10(^{-3})</td>
</tr>
<tr>
<td>550</td>
<td>6</td>
<td>98</td>
<td>6x10(^{-1})</td>
</tr>
</tbody>
</table>

Figure 6: The conversion for the cobalt catalyst remained active and stable for over 80 minutes.
Figure 7: The selectivity for the cobalt catalyst remained high over time and the catalyst did not reduce.

Dimerization of Ethylene

To test for oligomerization, which is a chaining reaction of hydrocarbons, a low-pressure reaction with pure ethylene was run to dimerize ethylene. As shown in Table 3, low conversions (~3%) to C4 products were identified and higher molecular weight hydrocarbons from oligomerization were also present. At higher pressures, liquid products are expected to form.

Table 3: C2H4 dimerization was performed on Co2+/SiO2 (1 atm, 400-500°C)

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>X (%)</th>
<th>C4 (%)</th>
<th>&gt; C4 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2</td>
<td>63</td>
<td>37</td>
</tr>
<tr>
<td>450</td>
<td>2</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>500</td>
<td>4</td>
<td>68</td>
<td>32</td>
</tr>
</tbody>
</table>

Discussion:

Nickel on zeolites (Ni2+/BEA) is a known oligomerization catalyst, and Nickel on silica (Ni2+/SiO2) was recently stabilized at high temperatures in the form of (Ni-P/SiO2) for alkane dehydrogenation. Unlike nickel on silica, which reduces at high temperatures, single site cobalt was stable at temperatures up to 550°C for multiple hours. Both cobalt and nickel stabilized by phosphate performed dehydrogenation with high stability and selectivity, with nickel having an initial conversion of 18% at 600°C. In comparison, cobalt had a conversion of 6% at a lower temperature. Conversion is expected to increase at higher pressures. The single site cobalt catalyst is also heterogeneous, meaning a solid catalyst is used for gaseous reactants and products. Traditional industrial catalysts are often homogeneous catalysts, which have drawn scrutiny for having negative environmental impacts due to their low reusability and difficulty in separating products. In the catalysis field, there is a goal to develop heterogeneous catalysts that can be efficiently scaled up for commercial processes. The stable performance of the cobalt catalyst over multiple hours as shown in Figures 6 and 7 allow it to be considered on par with homogeneous counterparts in terms of stability.

Due to the shared reaction intermediate of a metal hydride, if a metal catalyst performs dehydrogenation, it is hypothesized to perform oligomerization as supported by data from these
nickel and cobalt catalysts. Based on the data from the hydrogenation tests, a correlated increase in TOF from a hydrogen pretreatment suggests that the H₂ pretreatment activates the catalyst and preforms a hydride intermediate prior to the start of the reaction. This aligns and further indicates that a M-H intermediate is formed through the dissociation of H₂. This is further supported by the dimerization results of C₂H₄. To achieve higher conversions than observed in the dimerization results, higher pressures are necessary.

**Conclusions and Future Work:**
A cobalt catalyst was successfully synthesized and active for propane dehydrogenation and oligomerization. The findings from the project support the proposal that the M-H intermediate is responsible for oligomerization. Therefore, it can be anticipated that other metals that form M-H will also facilitate oligomerization and may be studied to support this hypothesis. To screen for oligomerization, other metals may simply be tested for dehydrogenation. To further support the findings from the project, the cobalt catalyst will also be tested in a high-pressure reactor (up to 600 psi) to supplement the current oligomerization data. As the scope of this study was limited to providing a proof of concept, further studies are necessary to better understand and optimize the hypothesized processes occurring in this study to an industrial level. The environmental benefits will also be quantified, and the specific improvements to current catalyst efficiency will be further analyzed.