Catalytic Isomerization of α-Olefin to Internal Olefin

A low-temperature, fast-kinetic route to a clean internalized olefin

Alkenyl-substituted cyclic anhydrides are used extensively in the papermaking industry as an additive to improve the properties of paper, including fine paper, recycled linerboard and gypsum board. These compounds have reactive functional groups that are believed to covalently bond to cellulose fibers and hydrophobic tails that are oriented away from the fibers, allowing the paper to repel water. Commercial-sizing agents based on alkenyl succinic anhydride (ASA) are typically prepared from maleic anhydride and one or more internal olefins (e.g., C_{16} or C_{18} olefins), which are made from the alpha olefin.

The internal olefins are usually generated by isomerization of the corresponding α-olefins using homogeneous or heterogeneous acids as the catalyst. This process has disadvantages including the fact that the isomerization step can only be performed at relatively high temperatures and can often lead to skeletal rearrangements. In addition, before they can be reacted with maleic anhydride to form ASA compounds, the obtained isomerized olefins must be cleaned by distillation to remove undesired catalyst complexes and coloring caused by decomposition products. Also, this reaction is better suited for conditions where it is not exposed to direct light, the air is thoroughly removed, and the reaction is kept under pressure. These disadvantages add time, complexity and cost to the process.

In comparison, SiGNa’s sodium-supported base catalyst offers a significant process improvement that speeds kinetics and reduces temperature requirements; this process, which can be used in either batch or continuous production runs, offers the ability for users to increase throughput and reduce the costs associated with the making and use of alkenyl-substituted cyclic anhydrides.

SiGNa’s Sodium-Base Catalyst

SiGNa Chemistry has exclusively licensed a sodium-supported base catalyst from ExxonMobil Chemical for use in all olefin isomerization reactions. This catalyst provides a de-protonation-protonation process that converts the terminal olefin to the more thermodynamically-stable internal olefin.

SiGNa’s catalyst, when used to isomerize an α-olefin, provides the following benefits:

<table>
<thead>
<tr>
<th>Catalyst Loading</th>
<th>&lt; 1.0 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>23 – 40°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Kinetics (batch)</td>
<td>60 – 120 mins</td>
</tr>
<tr>
<td>Location</td>
<td>Random position</td>
</tr>
<tr>
<td>Rxn Workup</td>
<td>No purification step required</td>
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</tbody>
</table>

Experimental Section

The intent of SiGNa’s trials was to check the products, reaction yields, reaction kinetics and catalyst lifetime for internal olefin formation resulting from the catalytic isomerization of the liquid α-olefin. The experiments described in this report were designed to test the proof-of-concept reaction conditions on 100 mL batches of α-olefin with various catalyst loadings (1 wt.% and 2 wt.%) as well as possible flow studies for continuous processing.

Batch Isomerization Studies

The first runs with both 1 wt.% and 2 wt.% catalyst were performed at room temperature with 100 mL of the α-olefin as received. Although the samples were covered with nitrogen during the run, they were not de-aerated by bubbling nitrogen through the liquid olefin. As a result, the 1 wt.% catalyst was completely ineffective, but the 2 wt.% catalyst concentration resulted in greater than 85% conversion in 30 minutes, as seen in Figure 1.

Figure 1. Neat α-olefin isomerized with 2 wt.% catalyst.
To enhance the catalyst efficacy in converting the as-received \(\alpha\)-olefin, the next runs were made with 100 mL samples of \(\alpha\)-olefin that were de-aerated by gentle \(N_2\) bubbling. The result was that, even with only 1 wt.% catalyst, greater than 98% of the \(\alpha\)-olefin was isomerized. Figure 2(A) shows the time-course of the initial run and Figure 2(B) shows the change in intensity of the two peaks that are characteristic of the \(\alpha\)-olefin as well as the ratio of these peak intensities to those that remain constant during the run. For this experiment, the two methods of following the isomerization are essentially the same, but in other runs the ratio method is clearly superior.

The reaction of purged olefin with 1 wt.% catalyst at room temperature is relatively fast. Another run was made with \(N_2\)-purged olefin with 1 wt.% catalyst loading, but the temperature was raised to 40°C. As shown in Figures 3, the reaction rate was nearly the same as the reaction rate at room temperature, but the reaction isomerization was more complete. The final spectrum shows essentially complete conversion, with a maximum of 0.75% residual \(\alpha\)-olefin.

To test the temperature dependence of the reaction rate, an attempt was made to carry out the reaction at 0°C by immersing the reaction flask in an ice-water mixture. This run was made with 2% catalyst content. A problem arose from the fact that the \(\alpha\)-olefin freezes at about 15°C, while the isomerized olefin is still liquid at 0°C. In spite of the presence of frozen material on the wall, the reaction was allowed to proceed for two hours with stirring and liquid sample removal at 15, 30, 45, and 60 min. The spectra are shown in Figure 4; they demonstrate that the reaction proceeds to completion at 0°C even though some material is frozen on the wall of the vessel during reaction.

**Batch Isomerization Analysis**

From the results described above, it appears that the catalyst becomes less effective without careful outgassing by purging with nitrogen. Since the catalyst is a very strong base, any acidic impurities, even those with high \(pK_a\) values, could reduce its basicity to the point that the catalyst would no longer affect H-atom transfers (e.g., water would probably act as a catalyst poison.)
To determine whether the conversion of water and other proton-donating impurities to higher pKₐ materials would increase the catalyst lifetime, the starting olefin was first purged with nitrogen and then stirred with SiGNa’s stabilized sodium in alumina gel (Na-AG) for 1 hour to remove all water. The liquid (100 mL) was removed from the Na-AG and stirred with 1 wt.% catalyst at room temperature for 2 hours, with sampling at various times intervals. The time-evolution of the IR spectrum is shown in Figure 5(A) and the fraction of α-olefin remaining as a function of time is shown in Figure 5(B).

Pre-treatment of the α-olefin using SiGNa’s Na-AG clearly increases the rate of conversion and yielded an IR spectrum virtually identical to that of the isomerized olefin. The exposure to Na-AG for just 1 hour decreased the extent of catalyst diminishing, as indicated by comparison with the earlier tests that had just been N₂-purged. After about 15 minutes and the conversion of about 20 % of the additional 100 mL of α-olefin, the reaction stops (total of 0.83 wt.% catalyst).

This continued isomerization could be due to effective removal of impurities by the intimate mixture of catalyst and Na-AG. The reaction rate in the recycled run is substantially slower than that in the first run, but the decrease in α-olefin concentration continued throughout the 2 hour period. A comparison of the time courses for the two runs is shown in Figure 6.

Flow Reaction

It would have been useful to be able to carry out the isomerization reaction in a flow system. However, to have sufficient length to demonstrate the reaction progress during flow for passage through a sample of 0.75 wt.% catalyst (based on 100 mL of olefin), the reaction would require the use of either a small diameter column or a very large amount of olefin. To limit the work to 100 mL of olefin, SiGNa used a ¼-inch glass column (inside diameter ~4.5 mm). This gave a column length of 7 cm. Because of the reactor’s small diameter, it was necessary to use N₂ pressure to force the liquid through the column permitting...
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Figure 8. Time course comparison of both 100 mL of N₂-outgassed olefin using the same 1.0 wt.% and 1 wt.% Na-AG at RT.

A flow rate of only 0.125 mL/min. The olefin was completely converted in just 5 mins of residence time on the catalyst bed.

All samples tested over a 2-hour time span showed complete convergence of the α-olefin to the isomerized olefin, showing that passage through a column provides very fast and complete isomerization.

Conclusion

As described, SiGNa has tested the effectiveness of isomerization in a batch mode under various conditions. Simply outgassing the olefin by purging with nitrogen seems to limit the yield to about 100 grams of isomer per gram of catalyst. The reaction is fast at room temperature and should be amenable to continuous flow methods.

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