Quarterly Status Report

Molecular Catalytic Coal Liquid Conversion

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Abstract

In this Quarter, the research was focused continually on the two general tasks: Task 1, molecular organometallic catalysts for hydrogenation and Task 2, organic base catalysts for arene hydrogenation and the hydrotreating of the coal liquids.

With regards to Task 1, the $[1,5$-HDRhCl]$2/buffer catalyst system has been investigated in detail to improve its performance. In the presence of CTAB ([CTAB]/[Rh]=2.0), the stability of the catalyst was improved greatly. The relationship between the turnover number of the catalyst (the moles of hydrogenated substrate per mole of Rh catalyst) and the reaction time was obtained. After 8 days in which the same catalyst was used for 8 cycles, there was no decrease in catalytic activity. The turnover numbers of the catalyst increases linearly with the reaction time in this period and reaches about 1350. Other aromatic compounds such as toluene, $n$-butylbenzene, tetralin, o-xylene all can be hydrogenated into the corresponding substituted cyclohexane derivatives in more than 94% yields when catalyzed by $[1,5$-HDRhCl]$2$ in the presence of small amount of surfactent molecules. The optimum catalyst system has been applied for the hydrogenation of tetralin in the presence of a coal liquid derived from the coal liquefaction. It was found that about 80-85% of tetralin in the mixture was hydrogenated to decalin under the conditions of these experiments.

Task 2 was continually focused on the hydrogenation of coal liquids. Institution of dideuterium for dihydrogen in the hydrotreating of coal liquid at 250 °C and 1000 psig of dideuterium yielded a product that was characterized by $^2$H NMR. Two groups of deuteron located in the region of 6.5 - 8.0 ppm and 1.0 - 3.5 ppm, respectively, were observed. The former group was assigned to the deuterons on carbon atoms of aromatic rings and the latter to the deuterons linked to the aliphatic carbon atoms. In addition, naphthalene was hydrogenated completely to tetralin in the presence of the coal liquid under the same conditions, implying that the reduction of multiaromatic compounds was not adversely influenced by the existence of the coal liquid which contains potential catalyst poisons such as sulfur, nitrogen and oxygen.

Introduction

Research work has concentrated continually on the two general tasks that were described in the original proposal. The first task concerns the development of molecular organometallic homogeneous catalysts that can be eventually used in...
the hydrogenation of coal liquids. The second task concerns non-metallic organic bases that can activate dihydrogen for arene hydrogenation, and that can be used in the hydrotreating of coal liquids.

**Results and Discussion**

**Task 1 Molecular Organometallic Catalytic Reactions**

In the last Quarter's report, we showed that the catalytic performance especially the stability of the $[1,5\text{-HDDR}h\text{Cl}]_2$/buffer catalyst system can be improved by the addition of a small amount of a surfactent molecule such as cetymethylammonium bromide (CTAB) or tetrabutylammonium hydrogen sulfate (THS). In the presence of CTAB ($[\text{CTAB}]/[\text{Rh}] = 2.0$), the stability of the catalyst was improved greatly. The relationship between the turnover number of the catalyst (the moles of hydrogenated substrate per mole of Rh catalyst) and the reaction time is shown in Fig. 1. After 8 days in which the catalyst was used for 8 cycles, there was no decrease in catalytic activity. The experimental turnover number of the catalyst increased linearly with the reaction time in this period and reached about 1350. Hence, an active, stable catalyst system was found for the hydrogenation of aromatic compounds under mild conditions. In addition, the catalyst can be easily separated from the system and the noble metal (rhodium) can be collected and reused.

Table 1 shows our results for the hydrogenations of other aromatic compounds catalyzed by $[1,5\text{-HDDR}h\text{Cl}]_2$ in the presence of surfactent molecules. Substituted benzenes such as toluene, $n$-butylbenzene, tetralin, o-xylene all can be hydrogenated into the corresponding substituted cyclohexane derivatives in more than 94% yield. Multiaromatic compounds such as naphthalene also can be reduced to a mixture of cis- and trans-decalins with the cis-/trans-isomer ratio of
It was found that tetralin was an intermediate in the hydrogenation process, but no tetralin was detected by GC after the reaction was completed. m-Dimethoxybenzene was hydrogenated to the m-dimethoxycyclohexane in 98% yield. The product was a mixture of cis- and trans-isomers with the cis/trans isomer ratio of about 1:1. This result imply that the catalyst system was effective for the reduction of electron rich benzene rings and inert to the oxygen-containing ethers in the reaction system.

The optimum catalyst system has been applied for the hydrogenation of tetralin in the presence of coal liquid derived from the coal liquefaction. Fig. 2 is the $^1$H NMR spectra of the mixture of tetralin/coal liquid(12.5 wt % of coal liquid) before (a) and after being hydrogenated (b). Quantitative analysing proton NMR data showed that about 80-85% of tetralin in the mixture was hydrogenated to decalin under the experimental conditions ([tetralin]/[Rh]= 200, [aqueous phase]/[organic phase] = 0.3, [CTAB]/[Rh] = 2.0), implying that the catalyst system can be operated smoothly even in the existence of some poisonous elements such as sulfur, nitrogen and oxygen that are commonly present in the coal derived liquids.

Other factor which affect the catalyst’s performance such as the stirring method were also investigated. Mechanical stirring is more effective than magnetic stirring or mechanical shaking.

**Task 2 Organic base-catalyzed arene hydrogenation and the coal liquid hydrotreatment**

In the last Quarter, the research was focused on the hydrotreating of coal liquid (VSOH) catalyzed by lithium diisopropylamide and potassium bis(trimethylsilyl)amide. The dependence of temperature and hydrogenation pressure on the hydrotreating of VSOH was investigated systematically. The coal
liquid that was hydrotreated at 300 °C has an H/C ratio of 1.53 while that treated at 100 °C has an H/C ratio of only 1.43. We found that 1000 psig of hydrogen pressure was needed for the reaction to proceed completely. Other catalytic alkali metals were also used to hydrotreat the same coal liquid. Potassium bis(trimethylsilyl) amide was more active than lithium bis(trimethylsilyl)amide and sodium bis(trimethylsilyl)amide.

In this quarter, more experiments on the hydrotreating of coal liquids with the organic base catalyst systems have been conducted. Institution of dideuterium for dihydrogen in the hydrotreating of coal liquid at 250 °C and 1000 psig of dideuterium yielded a product which was characterized by ²H NMR as shown in Fig. 3. Two groups of deuterons located in the region of 6.5 - 8.0 ppm and 1.0 - 3.5 ppm, respectively, were observed. The former group was assigned to the deuterons in the carbon atoms of aromatic rings and the latter to the deuterons bonded to aliphatic carbon atoms. There are two sources for these deuterons, one is from the reduction of the aromatic compounds and another is from the D-H exchange. As we concluded in the previous report, in which naphthalene was reduced catalytically by potassium bis(trimethylsilyl)amide with dideuterium instead of dihydrogen, the D-H exchange reaction occur simultaneously with the reduction of the aromatic compounds, or the reduction of the aromatic compounds was accompanied by the D-H exchange. The deuterons in the aromatic region came from the D-H exchange during the reduction process and the deuterons in the aliphatic region came from either the reduction of aromatic compounds or the D-H exchange during the reduction process. The experiments in which naphthalene was hydrogenated completely in the presence of coal liquid under the same conditions implied that the reduction of multiaromatic compounds was not influenced by the existence of coal liquid which contains some potential poisoning elements such as sulfur, nitrogen and oxygen. Thus, the multiaromatic hydrocarbons in the coal liquids were catalytically hydrogenated by the strong
organic bases under the experimental conditions.

As mentioned above, the hydrogenation of naphthalene to tetralin in the presence of coal liquids has been investigated in order to identify how effective the catalyst is for the reduction of polycondensed aromatic hydrocarbons in the coal liquids. The result indicate that 2.0g of naphthalene in 10g of VSOH was hydrogenated completely at 250 °C under 1000 psig of hydrogen.

Plan for Next Quarter

The work will continue to focus on the two tasks. More work will be needed in the rhodium catalyst system to improve the catalyst performance and to test the application of this catalyst system for the hydrotreating of coal liquids. The investigation of hydrotreating of coal liquids catalyzed by organic bases will proceed in parallel.
Table 1 The hydrogenation of aromatic compounds catalyzed by [1,5-HDRhCl]2

<table>
<thead>
<tr>
<th>No</th>
<th>Substrate</th>
<th>Product(%)</th>
<th>Total(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>tetralin</td>
<td>trans-decalin (21), cis-decalin (79)</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>naphthalene</td>
<td>trans-decalin (13), cis-decalin (87)</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>o-xylene</td>
<td>1,2-dimethylcyclohexane (94)</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>methylcyclohexane (100)</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>m-dimethoxybenzene</td>
<td>m-dimethoxycyclohexane (98)</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>n-butylbenzene</td>
<td>n-butylcyclohexane (75)</td>
<td>75</td>
</tr>
</tbody>
</table>

Conditions: substrate: 25.0 mmole; [1,5-HDRhCl]2 (58 mg, 0.126 mmole) [substrate]/[Catalyst]: 200 : 1; solvent: hexane (30 ml) buffer(pH=7.4): 10 ml; [aqueous phase]/[organic phase](v/v): 0.30 CTAB at [CTAB]/[Rh] = 2.0; temperature: 25 °C; H₂ pressure: 1 atm
Fig. 1 Effect of reaction time on the catalytic activity of a Rh catalyst that is stabilized by CTAB.

Reaction conditions: [CTAB]/[Rh] = 2, others seen in Table 1
Fig. 2 $^1$H NMR spectra of a coal liquid and tetralin mixture before (a) and after being hydrogenated (b). The very large decrease in the tetralin to coal liquid ratio establishes the reaction has proceeded successfully.
Fig. 3 $^2$H NMR spectrum of hydrotreated coal liquid with dideuterium catalyzed by potassium bis(trimethylsilyl)amide under 1000 psig of D$_2$ at 250 °C

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