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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 biphasic catalyst system, $[1,5\text{-H}2\text{RhCl}]_2/\text{buffer}$, was investigated in detail for the hydrogenation of naphthalene or tetralin to decalin under low pressure of H_2 at room temperature. The influence of various factors such as the amount of the phase transfer reagent, the volume ratio of the organic phase to the aqueous phase, the pH value and compositions of the buffer solution as well as the solvents on the reaction process was investigated systematically. It was found that the rhodium catalyst works well under biphasic conditions rather than under phase transfer conditions. Apparently, the surfactant molecules negatively affect the catalytic activity of the rhodium catalyst. The pH values and the compositions of the buffers in the aqueous phase are critical in the system. The best buffer solution is composed of hydron with its pH of 7.4-7.6. In addition to tetralin, the Rh catalyst is also effective for the hydrogenation of other unactivated aromatic hydrocarbons such as toluene, n-butylbenzene etc. In addition, the turnover numbers of the catalyst can reach 200, but its performance needs to be improved further for practical applications. The work on this issue is currently underway.

Task 2 was focused on the hydrotreating of coal liquid (VSOH) catalyzed by Catalyst 2 and Catalyst 5. Good results were achieved on this issue. Catalyst 5 was found to be a more effective catalyst for the hydrotreating of coal liquid than Catalyst 2. The coal liquid was hydrotreated to give a clear yellow liquid under

relative mild conditions (1000 psi of hydrogen and 200 °C) if only 16 mol% of the Catalyst 5 was employed. The carbon content of the hydrotreated VSOH decreased while the hydrogen content increased dramatically as compared with the untreated sample.

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 used in the hydrogenation of coal liquids. The second task concerns non-metallic organic bases which 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 described some preliminary results on the catalytic properties of a rhodium catalyst for the hydrogenation of tetralin to decalin at room temperature and one atmosphere of H₂ under biphasic conditions. In this Quarter, this biphasic catalyst system, [1,5-HDRhCl]₂/Buffer, was investigated thoroughly.

Alper et al.¹ reported that the hydrogenation of aromatic hydrocarbons and heterocyclic compounds by using the dimer of chloro(1,5-hexadiene)rhodium

proceeded only under phase-transfer conditions, in which the phase transfer agents were tetrabutylammonium hydrogen sulfate (THS) or cetyltrimethylammonium bromide (CTAB) and the aqueous phase was a buffer solution with pH of 7.4 - 7.6. This catalyst system was investigated in more detail in our laboratory using tetralin as the substrate. Table 1 shows the effect of the quantity of surfactant (THS) used in the system on the conversion of tetralin to decalin with the mole ratio of [substrate]/[catalyst] equal to 200:1. It can be seen that addition of surfactant molecule into the reaction system reduces the conversion of the substrate. Only 40% of the conversion remained when the [THS]/[catalyst] mole ratio was 16 as compared with the system without any surfactant added. The same results were obtained if other surfactants such as dodecylsulfate sodium and Aliquat 336 were employed in the system. Hence, the $[1,5\text{-HDRhCl}]_2/\text{Buffer}$ catalyst system seems to be more effective under biphasic conditions than under phase transfer condition for the challenging hydrogenation of tetralin to decalin.

Table 2 shows the effect of the aqueous phase to organic phase volume ratio on the biphasic hydrogenation of tetralin to decalin without any surfactant employed. The biphasic system works well in a relatively broad range of organic phase to aqueous phase ratios (0.15 - 0.60). Under these conditions more than 78% of tetralin can be hydrogenated to decalin (No. 2, 3 and 4). However, the reaction does not proceed in the single organic phase system (No. 1). If same volume of water was used instead of the buffer solution in the biphasic system while keeping the other conditions the same as in No.5, the conversion of tetralin (43.5%) decreased 50% compared with the result using the buffer as the aqueous phase.

The influence of the buffer as aqueous phase on the tetralin hydrogenation is shown in Table 3. The pH as well as the composition of the buffer are both critical in the system. The buffers with same compositions but different pH values and those with same pH value but different compositions all yield different

conversions of substrate. For instance, the catalyst systems that employed a buffer with higher (No.3, pH=8.0) or lower (No.2 pH=7.0) pH values all yielded only half of the conversion of that employed in a buffer with pH=7.40. On the other hand, the catalyst system with buffer (pH= 7.4) composed of hydron ensures the hydrogenation of tetralin to decalin in 91% yield while that with the buffer with the same pH value (pH=7.4) but composed of sodium phosphate (0.1M) only yielded 34% of decalin under the same conditions ([catalyst]/[substrate]= 0.005, [aqueous phase]/[organic phase]=0.3). The highest yield (91.1%) was obtained by using the hydron buffer (pH=7.4).

Organic solvents in the system also affect the reaction process (Table 4). Of the solvents investigated such as hexane, methylene chloride, chloroform, dimethylethylene oxide as well as alcohols, we found that aliphatic hydrocarbons with shorter chains such as hexane, cyclohexane, heptane are better solvents for this reaction. However, the aliphatic hydrocarbons with longer chains (>8 carbons, such as octane, hexadecane etc.) had decreased conversions. These results may be impacted by the higher viscosity of these hydrocarbons which may reduce the mobility of the active catalytic centers in the biphasic system.

Except for tetralin, other aromatic compounds were also tested using the optimum catalyst system (Table 5). The hydrogenation of aromatic compounds were influenced importantly by the substituents in the aromatic ring. The ease of the hydrogenation of benzene, toluene, o-xylene, and mesitylene and tetralin were compared and found to be in the order benzene, toluene > n-butylbenzene > o-xylene > mesitylene.

The stability of the [1,5-HDRhCl]₂/Buffer biphasic system was superior to those reported previously². The turnover numbers of the catalyst (i.e., moles of aromatic compounds/moles of catalyst employed) reaches 200. However, this feature also needs to be improved further for the practical uses. The work on this issue is currently underway. The application of this catalyst system to the hydro-

treatment of coal liquids will be in the next quarter.

Task 2 Organic Base-catalyzed Arene Hydrogenation and The Coal Liquid Hydrotreatment

In last Quarter's report, we described preliminary results of the hydrotreatment of coal liquids catalyzed by Catalyst 2. In this Quarter, this issue has been investigated systemically and the results will be reported in the following section.

The hydrotreating of coal liquids supplied by The Department of Energy (Sample VSOH) has been investigated by using the organic base catalysts studied previously for the hydrogenation of model compounds such as naphthalene. The results are shown in Table 6. Two catalysts were tested for the hydrotreatment of the coal liquids (Sample VSOH): Catalyst 2 and Catalyst 5. With regard to the Catalyst 2, three experiments with various catalyst loadings ($[VSOH]/[catalyst]$ (g/g) = 10/1, 10/2, and 10/4) were performed. The conversion of the sample was calculated from the decrease in intensity of the absorptions at 321 and 338 nm in UV-Visible spectrum with increasing $[VSOH]/[catalyst\ 2]$ ratios(g/g). Conversions as high as 82 % at 338 nm and 97 % at 321 nm of conversion were obtained if 4 g of Catalyst 2 per 10 g of coal liquids was employed. Meanwhile, the elemental analysis for the product obtained under the same conditions indicates that carbon content (89.13) decreased 0.45 units and the hydrogen content (10.70) increased 0.62 units, thus the H/C ratio increased 0.074 from 1.357 to 1.431, as compared with the unhydrotreated coal liquid sample.

Compared with Catalyst 2, Catalyst 5 was found to be a more effective catalyst for the hydrotreating of this coal liquid. The coal liquid (VSOH) was hydrotreated to form a clear yellow liquid under mild conditions (1000psig of hydrogen and 200 °C) if 16 mol% of catalyst 5 was employed. The peaks in the

region of 8.0 - 8.3 ppm in ^1H NMR spectrum of the product, which are attributed to the protons in the polycondensed aromatic rings disappeared completely meanwhile new absorptions in the region of 1.5-3.5 ppm in ^1H NMR attributed to the protons in aliphatic carbons appeared (Fig.1, a typical NMR spectra of the hydrotreated coal liquids). In addition, the absorptions at 321nm and 338 nm, respectively, in UV-Visible spectrum which are attributed to the $\pi - \pi$ absorptions of polycondensed aromatic hydrocarbons also completely disappeared, indicating that all the polycondensed aromatic compounds such as naphthalene derivatives were hydrogenated to the monoaromatic hydrocarbons. The effect of temperature, catalyst loading as well as hydrogen pressure on the hydrotreating of coal liquids has been studied. In general, after being hydrotreated, the coal liquid has a lower carbon content and higher hydrogen content than the untreated coal liquid sample. For instance, the treated coal liquid obtained under a conditions (1000 psig of hydrogen and 300 °C with 16 wt.% catalyst loading) has an elemental analysis: C,88.38; H,11.36; H/C= 1.532, while that of untreated coal liquid: C, 89.58; H, 10.18; H/C= 1.357. In comparison, a 1.2% of decrease in carbon and 1.18 % of increase in hydrogen for the hydrotreated coal liquid was obtained, corresponding to the H/C ratio increase of 0.175.

Plan for Next Quarter

The work will continue to focus on these two Tasks. More work will be needed in the biphasic rhodium catalyst system to improve the catalyst performance and to apply this catalyst system for the hydrotreating of coal liquids. The investigation of hydrotreating of coal liquids catalyzed by organic bases will proceed in parallel.

References:

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Table 1 Effect of surfactant THS on the conversion of tetralin to decalin catalyzed by [1,5-HDRhCl]₂ catalyst

No	[THS]/[Catalyst] (mole/mole)	Yield(%)		
		<i>Trans</i> -decalin	<i>Cis</i> -decalin	Total
1	0.0	14.5	69.7	84.2
2	8.0	10.7	49.2	59.9
3	16.0	4.5	29.7	35.2
4	32.0	4.4	25.3	29.7

Conditions:

Substrate: Tetralin(3.3g, 25.0 mmole)
Catalyst: [1,5-HDRhCl]₂ (58 mg, 0.126 mmole)
[Substrate]/[Catalyst]: 200 : 1
Solvent: Hexane(30 ml)
Buffer(pH=7.4): 20ml
[Aqueous phase]/[Organic phase](v/v): 0.60
Temperature: 25 °C
H₂ pressure: 1 atm
THS: Tetrabutylammonium hydrogen sulfate

Table 2 Effect of the ratio of aqueous phase to organic phase on the biphasic hydrogenation of tetralin to decalin catalyzed by [1,5-HDRhCl]₂ catalyst

No	[Aq. phase]/ [Org. phase] (v/v)	Yield(%)		
		<i>Trans</i> -decalin	<i>Cis</i> -decalin	Total
1	0.0	<0.1	<0.4	<0.5
2	0.03	4.0	30.2	34.2
3	0.15	12.4	65.9	78.3
4	0.30	17.6	73.5	91.1
5	0.60	14.5	69.7	84.2
6*	0.60	5.7	37.8	43.5

Conditions:

Substrate: Tetralin(3.3g, 25.0 mmole)
Catalyst: [1,5-HDRhCl]₂ (58 mg, 0.126 mmole)
[Substrate]/[Catalyst]: 200 : 1
Solvent: Hexane(30 ml)
Buffer(pH=7.4)
Temperature: 25 °C
H₂ pressure: 1 atm

* Water was substituted for the buffer while keeping the other conditions the same as in No. 5

Table 3 Influence of the buffer as the aqueous phase on the biphasic hydrogenation of tetralin to decalin catalyzed by [1,5-HDRhCl]₂ catalyst

No	Buffer (pH, composition)	Yield(%)		
		<i>Trans</i> -decalin	<i>Cis</i> -decalin	Total
1	Buffer (pH=7.4, Hydrion)	17.6	73.5	91.1
2	Buffer (pH=7.0, Hydrion)	6.8	32.3	39.1
3	Buffer (pH=8.0, Hydrion)	4.6	32.8	37.1
4	Buffer(pH=7.4 phosphate(0.1M))	5.8	28.5	34.2
5	Buffer(pH=7.4, Phosphate:0.001M, NaCl: 0.138M KCl: 0.027M Tween 20: 0.05 % w/v)	4.4	36.1	40.5
6	Buffer(pH=7.4, Trizma saline: 0.05M NaCl: 0.56 %)	3.3	25.1	28.4

Conditions:

Substrate: Tetralin(3.3g, 25.0 mmole)
Catalyst: [1,5-HDRhCl]₂ (58 mg, 0.126 mmole)
[Substrate]/[Catalyst]: 200 : 1
Solvent: Hexane(30 ml)
Buffer: 10 ml
[Aq.phase]/[Org. phase]: 0.30
Temperature: 25 °C
H₂ pressure: 1 atm

Table 4 Effect of the organic phase on the biphasic hydrogenation of tetralin to decalin catalyzed by [1,5-HDRhCl]₂ catalyst

No	Solvent	Yield(%)		Total
		<i>Trans</i> -decalin	<i>Cis</i> -decalin	
1	Hexane	17.6	73.5	91.1
2	Methylene chloride	3.1	17.6	20.7
3	Chloroform	<0.1	6.2	6.3
4	CH ₃ O(CH ₂) ₂ OCH ₃	2.7	15.2	17.9
5*	Octane	4.8	26.7	31.5
6*	Hexadecane	2.0	8.1	10.1

Conditions:

Substrate: Tetralin(3.3g, 25.0 mmole)
Catalyst: [1,5-HDRhCl]₂ (58 mg, 0.126 mmole)
[Substrate]/[Catalyst]: 200 : 1 (* 400 : 1)
Solvent: 30 ml
Buffer(pH=7.4): 10ml
[Aqueous phase]/[Organic phase](v/v): 0.30
Temperature: 25 °C
H₂ pressure: 1 atm

Table 5 The hydrogenation of aromatic compounds
catalyzed by [1,5-HDRhCl]₂ catalyst

No	Substrate	Product(%)
1	tetralin	<i>trans</i> -decalin(17.6), <i>cis</i> -decalin(73.5)
2	naphthalene	tetralin(49.2), decalin(7.2)
3	toluene	methylcyclohexane(100)
4	O-xylene	1,2-dimethylcyclohexane(48.2)
5	mesitylene	1,3,5-trimethylcyclohexane(12.4)
6	n-butylbenzene	n-butylcyclohexane(75.4)

Conditions:

Substrate: Tetralin(3.3g, 25.0 mmole)

Catalyst: [1,5-HDRhCl]₂ (58 mg, 0.126 mmole)

[Substrate]/[Catalyst]: 200 : 1

Solvent: Hexane(30 ml)

Buffer(pH=7.4): 10ml

[Aqueous phase]/[Organic phase](v/v): 0.30

Temperature: 25 °C

H₂ pressure: 1 atm

Table 6 The hydrotreating of coal liquid(VSOH) catalyzed by Catalyst 2 and Catalyst 5

Catalyst	[VSOH]/ [Catalyst] (g/g)	Temperature (C)	Yield (%)	Conversion(%)		Elementat analysis		
				321nm	338nm	C	H	H/C
	VSOH			0.0	0.0	89.58	10.18	1.357
	VSOH	200	95.0	0.0	0.0	89.01	10.32	1.382
2	10/1	300	82.4	21.5	16.5	88.71	10.51	1.412
	10/2	300	80.8	76.7	62.3	88.98	10.66	1.428
	10/4	300	76.0	96.7	81.8	89.13	10.70	1.431
5	10/1	200	90.2	48.0	32.5	89.06	10.48	1.402
		300	88.4	98.0	91.2	89.27	10.70	1.428
	10/2	200	86.7	100	100	88.17	10.74	1.452
		300*	95.0	100	100	88.38	11.36	1.532
	10/2	200**	94.0	100	100	88.17	11.19	1.512
		200*	84.1	100	100	89.10	10.76	1.439

Conditions:

Solvents: Hexane for Catalyst 2 and
Hexane-toluene mixture(2/3 v/v) for
Catalyst 5

Reaction volume: 50 ml

Hydrogen pressure: 1000 psig at 25 °C

Reaction time: 24 hr

* Reaction time : 6hr

** H₂ pressure: 1300 psig

Fig. 1(a) ^1H NMR spectra of a) unhydrotreated and b) hydrotreated coal liquid(VSOH) catalyzed by Catalyst 5 at 200 °C and 1000 psi of hydrogen

Fig. 1(b) ^1H NMR spectra of a) unhydrotreated and b) hydrotreated coal liquid(VSOH) catalyzed by Catalyst 5 at 200 $^{\circ}\text{C}$ and 1000 psi of hydrogen