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Selective, Catalytic Decomposition of Hydrazine

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Selective, Catalytic Decomposition of Hydrazine

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The University of Akron Honors College

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Executive Summary

The selective, catalytic decomposition of hydrazine can provide an economically and environmentally effective method to produce hydrogen gas that can be used for a multitude of energy and fuel applications. Currently, many different catalyst systems exist for the decomposition of hydrazine. One disadvantage of many of these catalyst systems is the use of expensive noble metals. While these noble metals provide beneficial catalyst properties for hydrazine decomposition, their cost reduces the commercial prospects of the catalysts. The catalyst investigated in this report was a 1 wt% platinum supported on a nickel hydroxide nanosheet (1 wt% Pt-Ni(OH)₂). The goal was to investigate catalyst performance and determine how it compared to other catalysts with a high weight percent of noble metal.

The following factors were examined on the catalyst; reaction solution alkalinity, reaction temperature, selectivity, stability, and durability. Based upon the information displayed in the data and results section of the report, the optimal reaction alkalinity was found to be 1 M NaOH. Increasing the alkalinity of the reaction solution has been shown to increase catalyst activity in the decomposition of hydrazine. The optimal reaction temperature was found to be 50 °C. A reaction occurring above room temperature is undesirable, since the goal is to provide a catalyst capable of performing the reaction in a commercial setting at atmospheric conditions. The catalyst was found to be 100% selective in producing hydrogen and nitrogen gas. This means that no unwanted product of ammonia was formed from the partial decomposition of hydrazine. The catalyst showed promising stability showing no degradation in activity after two days in air and a small decrease in activity after eight days in air. To keep the cost of the catalyst down, the stability is important to reduce time between catalyst replacement or regeneration. Finally, the

durability tests showed relatively large activity decreases after successive reactions with the same catalyst. This decrease in activity is undesirable for the practicable use of the catalyst.

The design and testing of the 1 wt% Pt-Ni(OH)₂ catalyst provided an insight into the process of academic research. The process of choosing a research idea, performing in depth literature reviews, and ultimately testing a hypothesis via experimental work represents how the technology in the world advances. This specific research provided a possible method to produce hydrogen gas economically and safely. The relatively low cost due to a small amount of the noble metal platinum and the 100% selectivity that only produces clean nitrogen gas and usable hydrogen gas is a much needed system for society. The opportunity to replace many oil and coal fueled energy sources with clean running hydrogen fueled sources is an exciting step forward in technology. The chance to work on a project that can make an extreme impact on the world delivers strong interest and respect for the academic field.

Future work could be on further improvement to the current catalyst design. Some aspects of the catalyst such as the high optimal operating temperature and the low durability leaves room for improvement. If the catalyst were to be used commercially, not only reaction studies but economic studies would have to be completed. The feasibility of running the reaction on a larger scale under the optimal reaction conditions would determine the overall effectiveness of the catalyst in a specific application. If no economic promise was found, changes to the catalyst would need to be made such as increasing Pt weight percent or altering the metal used in the Ni(OH)₂ nanosheet. The capability to relate the academic research to practical applications provided a motivation for the project. It allowed additional questions to be asked furthering the experience gained from completing the research.

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Introduction

There is a strong demand for economically favored techniques to produce hydrogen gas for use in hydrogen fuel cell powered transportation, heat and power generation, and energy storage systems.¹ Transitioning to hydrogen energy sources as an alternative to oil derivatives is becoming more desired due to the strong environmental concerns oil presents.²⁻³ A current research method to produce hydrogen is the selective decomposition of hydrazine. Hydrazine, H₂NNH₂, is a promising candidate for hydrogen production due to having a respectively high hydrogen content of 12.5 wt% in the anhydrous form and 7.9 wt% in the hydrous form.⁴ The decomposition of hydrazine can follow two different reaction pathways seen in Equation 1 and Equation 2.⁵

$$H_2NNH_2 \to N_2(g) + 2H_2(g) \tag{1}$$

$$3H_2NNH_2 \to 4NH_3 + N_2(g) \tag{2}$$

The complete decomposition reaction seen in Equation 1 is desired over the incomplete decomposition reaction seen in Equation 2. Ammonia is an unwanted product in the reaction because it would require additional separation and recycling in commercial applications such as fuel cells and it could poison expensive fuel cell membranes and catalysts.⁶ Ammonia production also reduces the amount of usable hydrogen gas that can be produced from the hydrazine. Selectively following only Equation 1 allows the hydrogen gas to be utilized as an energy source and the nitrogen gas to be safely released to the atmosphere whilst remaining environmentally conscience.

The focus in the following research was to develop a catalyst system that is relatively inexpensive, stable, operates under close to standard temperature and pressure, and is highly selective in hydrogen and nitrogen production while avoiding the formation of ammonia. To be economically feasible, the catalyst needs to have a low cost. A major obstacle to overcome is the use of costly noble metals in the catalyst. The use of low noble metal content alloy catalyst as well as noble metal free catalyst will be investigated. The catalyst also needs to be stable to provide reliable function. A catalyst that degrades after a small number of uses would be of little benefit in commercial uses. The catalyst is desired to operate under close to standard temperature and pressure for use in on-board production of hydrogen. High pressure and temperature reactors are undesired when it comes to the use in markets such as cars. The end goal of a technology such as hydrogen production is a safe system that can be utilized by consumers. The high selectivity is crucial as aforementioned.

This report discusses a bimetallic Pt-Ni(OH)₂ catalyst system. Multiple factors were tested to determine the feasibility of the catalyst in terms of the aforementioned desired traits. The different tests ran on the catalyst are summarized in Table 1 below.

Table 1. Test Factors used to Characterize Catalyst Efficacy

Experimental Tests Reaction Solution Alkalinity Temperature Hydrazine Concentration Catalyst Selectivity Catalyst Stability Catalyst Durability

Each test produces the necessary information to determine if the catalyst is effective, can be run under standard conditions, highly selective in hydrogen and nitrogen, stable, and durable. All of these traits need to exist for a catalyst system to be feasible in commercial processes. The preparation, characterization, and testing of the catalyst was investigated as well as the rate laws which were determined via kinetic studies. Rate-limiting step and reaction mechanism was investigated via conducting mechanistic experiments. All of these calculations and observations were utilized to conclude if the catalyst is suited for the production of hydrogen and nitrogen from hydrazine.

Background

Many catalyst systems used for hydrazine decomposition utilize a bimetallic alloy involving a noble metal. These catalysts have strong selectivity in hydrogen, and can generally operate at ambient conditions. A common goal in current research is to design a catalyst system that reduces or eliminates the need for the use of noble metals.⁷⁻⁹ The issue with noble metal catalyst systems is the high cost associated with purchasing noble metal which, consequently, reduces the economic feasibility of a large scale system. Based on the work by Singh et al., bimetallic alloy combinations of nickel with a noble metals rhodium, platinum, and iridium provides successful results in terms of hydrogen selectivity. Their work looked into finding noble metal free catalysts that perform similarly to the noble metal catalyst system. The catalyst used was bimetallic nickel-iron. Good performance was achieved, but elevated temperature above 298 K were necessary for the catalyst to exhibit any reaction kinetics at all.

Another common practice in the decomposition of hydrazine is to perform the reaction in an alkaline solution, usually NaOH. The work done by Wang et al. shows the effects of NaOH on a graphene supported rhodium-nickel catalyst. Testing showed that washing the NaOH from the catalyst caused decreased selectivity and activity where the re-addition of NaOH caused the original catalyst performance to return. The NaOH is thought to increase the complete

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decomposition reaction and inhibit the formation of NH₃, therefore leading to 100% hydrogen selectivity.¹⁰

The work by Sanjay et al. shows a catalyst similar to the one investigated in this report with a bimetallic Ni-Pt nanocatalyst. Their research shows that under ambient conditions, the single component metals showed no activity for the partial or complete decomposition of hydrazine. When alloyed together, the two inactive metals produced a highly selective and active catalyst that even with relatively low concentrations of the noble metal platinum at 7 mol%. This Ni-Pt catalyst also showed a strong selectivity and activity at room temperature, which demonstrates that the complete decomposition into nitrogen and hydrogen is feasible without having to operate at high temperatures.¹¹

Experimental Methods

The 1 wt% Pt-Ni(OH)₂ catalyst was prepared using the following method. 2 mmol of nickel acetate tetrahydrate (Ni(CH₃CO₂)₂·4H₂O) and 4 mmol of hexamethylenetetramine (C₆H₁₂N₄) were dissolved in 35 mL of deionized water, covered with parafilm, and strongly stirred for 30 minutes. The mixed solution was transferred into a 40 mL autoclave and heated at 120 °C for 12 hours. Once removed from the heat source, the mixture was let to cool to room temperature. The mixture was centrifuged followed by washing with deionized water and ethanol. The centrifuge and wash step wash repeated 2 more times to completely wash the solids. The purified solids were then dried in a 60 °C oven overnight. The product of the aforementioned steps was the Ni(OH)₂ nanosheets used to support the Pt metal. The Pt metal was added to the nanosheet by first dissolving potassium hexachloroplatinate (K₂PtCl₆) in deionized water and then combining that solution with the dried Ni(OH)₂ nanosheets. The mixture was

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sonicated for 10 minutes, then a 0.1 M sodium borohydride (NaBH₄) solution was added dropwise into the mixture under strong stirring at room temperature. The solution was stirred for 15 minutes, then centrifuged and washed with deionized water 3 times similarly to the centrifuging process before. the solid product, 1 wt% Pt-Ni(OH)₂ was collected and dried overnight in a 60 °C oven.

The reaction was conducted in a semi-batch flask reactor charged with 30 mg of catalyst and 3 mL of deionized water. The two side flask openings were then sealed with an air tight rubber cap while the top opening was connected to an airtight gas burette. The burette was used to measure the exact amount of gaseous product produced during the reaction. The entirety of the reaction solution was submerged in a stirring oil bath held at a constant temperature via a temperature probe and heating controller. The reaction solution was stirred with a magnetic, Teflon stir bar. To begin the reaction, the hydrazine (N₂H₂) was injected into the flask through one of the rubber seals and the volume of evolved gas was measured versus time. For some experiments, an ammonia trap was placed between the reaction vessel and the burette.

Data and Results

The first test conducted on the Pt-Ni(OH)₂ catalyst was a variation in alkalinity of the reaction solution. The reaction was tested with different concentrations of NaOH in the reaction solution including 0 M, 0.5 M, 1 M, and 2M. These four cases were completed each at 50 °C, with 30 mg of catalyst, and a hydrazine concentration of 0.1 M. Figure 1 shows the results of the four different tests at varying NaOH concentrations. As the alkalinity increased, the hydrazine conversion increased drastically.



Figure 1. Hydrazine conversion versus time at different NaOH concentrations with a reaction temperature of 50 °C, 30 mg of Pt-Ni(OH)₂ catalyst, and a hydrazine concentration of 0.1 M.

The next test consisted of varying the reaction temperature. The temperature was varied from 20-60 °C in 10° increments. This test was conducted at a NaOH concentration of 1 M, which was chosen because it provided the optimal reaction condition in the initial catalyst study. The same catalyst amount of 30 mg was used as well as a hydrazine concentration of 0.1 M. Figure 2 shows the results of the five different tests at varying temperatures. As the reaction temperature was increased, the resulting hydrazine conversion greatly increased as well.



Figure 2. Hydrazine conversion versus time at varying reaction temperatures with a NaOH concentration of 1 M, 30 mg of Pt-Ni(OH)₂ catalyst, and a hydrazine concentration of 0.1 M.

Next, the concentration of hydrazine in the reaction vessel was investigated by running four tests at a hydrazine concentration of 0.05 M, 0.1 M, 0.2 M, and 0.3 M. Figure 3 shows the four different experiments at different hydrazine concentrations. As the hydrazine concentration increased, the hydrazine conversion decreased.



Figure 3. Hydrazine conversion versus time at varying concentrations of hydrazine with a reaction temperature of 50 °C, 30 mg of Pt-Ni(OH)₂ catalyst, and a NaOH concentration of 1 M.

The selectivity of the reaction was then investigated by running the reaction with and

without an ammonia trap. The two separate reactions can be seen below in Figure 4. The

hydrogen conversion of the two conditions was identical.



Figure 4. Hydrazine conversion versus time with and without an ammonia trap with a reaction temperature of 50 °C, 30 mg of Pt-Ni(OH)₂ catalyst, and a NaOH concentration of 1 M.

The stability of the catalyst was tested by comparing freshly made catalyst to catalyst that was 2 days and 8 days old. The 8 day old catalyst test was performed twice to ensure precise results. The resulting data can be seen in Figure 5, which, when compared to the fresh catalyst, shows decreased activity for the 8 day old catalyst, but similar activity for the 2 day old catalyst.



Figure 5. Hydrazine conversion versus time for fresh, 2 day, and 8 day catalyst with a reaction temperature of 50 °C, 30 mg of Pt-Ni(OH)₂ catalyst, and a NaOH concentration of 1 M.

The durability of the catalyst was tested by running consecutive experiments on the same batch of catalyst. Three reactions were run for the same catalyst batch and this process was repeated once. Figures 6 and 7 show the experimental results for the two separate durability tests. The results show that as the reaction is carried out on the same batch of catalyst, the activity begins to decrease for each cycle.



Figure 6. Hydrazine conversion versus time for cycling the catalyst three times with a reaction temperature of 50 °C, 30 mg of Pt-Ni(OH)₂ catalyst, and a NaOH concentration of 1 M.



Figure 7. Hydrazine conversion versus time for cycling the catalyst three times with a reaction temperature of 50 °C, 30 mg of Pt-Ni(OH)₂ catalyst, and a NaOH concentration of 1 M.

Finally, the catalyst being investigated, Pt-Ni(OH)₂, was compared to the two individual metals Ni and Pt in the form of Ni(OH)₂ and Pt-C respectively. Figure 8 shows the results comparing the hydrazine conversion versus time of the three different catalysts. The monometallic species exhibit minimal activity compared to the Pt-Ni(OH)₂ catalyst.



Figure 8. Hydrazine conversion versus time for Pt-Ni(OH)₂, Ni(OH)₂, and Pt-C catalyst with a reaction temperature of 50 °C, 30 mg of catalyst, and a NaOH concentration of 1 M.

Discussion/Analysis

To test the feasibility of the designed catalyst, 1 wt% Pt-Ni(OH)₂, six separate experiments were conducted. First the optimal concentration of NaOH in the reaction solution was found to be 1 M NaOH, which can be seen in Figure 1. Initially, increasing the alkalinity of the reaction solution from normal conditions, via addition of NaOH, greatly increased reaction conversion. A 0.5 M NaOH reaction solution reached about 74% hydrazine conversion after 15 minutes while the normal reaction solution with no NaOH only reached a hydrazine conversion of about 16%. The alkalinity was slowly increased until the increase in conversion became very small. Thus, the optimal NaOH concentration was found to be 1 M for the best reaction activity.

Next the reaction temperature was investigated with the results seen in Figure 2. As expected, the reaction conversion increases with increasing temperature. Ideally, the reaction would run efficiently at room temperature to reach 100% hydrazine conversion. The reaction occurring at room temperature would allow for the catalyst to be used much more effectively in energy production applications. Interpolating the data, the current catalyst design only reaches about 13% hydrazine conversion at a temperature of 25 °C. This low conversion means the catalyst is not optimal for commercial use and further work would need to be completed to produce a reaction that reaches 100% hydrazine conversion at room temperature. For the subsequent tests, a reaction temperature of 50 °C was chosen to elicit and 100% conversion reaction in a reasonable amount of time.

To determine the selectivity of the reaction, one reaction was run without an ammonia trap followed by an identical reaction run with an ammonia trap. As seen in Figure 4, there is no significant difference in the reaction run with and without the ammonia trap. This results shows that the 1 wt% Pt-Ni(OH)₂ catalyst shows 100% selectivity of hydrogen and nitrogen over ammonia. This result was verified with a gas chromatography (GC) analysis of the product gas. Figure 9 below shows the elution chromatogram where there is no apparent ammonia peak.



Figure 9. GC chromatogram of the product gas from the hydrazine decomposition reaction.

It is highly desirable that the catalyst favors the complete decomposition reaction into hydrogen and nitrogen seen in Equation 1 instead of the partial decomposition into ammonia and nitrogen seen in Equation 2. The complete decomposition allows for an economically and environmentally friendly catalyst due to the negative effects of the ammonia as described previously in the introduction of the report.

A key role in the functionality of the catalyst is the stability or the ability of the catalyst to remain active over periods of dormancy. This necessary catalyst feature was examined by letting the catalyst sit in air for two and eight days. As seen in Figure 5, the two day old catalyst exhibited no significant decrease in activity, generating 100% hydrazine conversion in the same amount of time as the fresh catalyst. The eight day catalyst did show a decrease in activity only reaching 85% hydrazine conversion at the same time that the fresh catalyst reached 100% hydrazine conversion. This activity decrease could be caused by the Pt particles on the catalyst agglomerating, effectively reducing the number of active Pt sites. A similar feature to stability, the durability of the catalyst needs to be high to reduce the need to replace or regenerate the catalyst. Figure 6 and Figure 7 show how the catalyst performed when run in consecutive reactions. After each reaction, the activity of the catalyst decreased, which is not desirable for a commercial hydrazine decomposition process. The catalyst needs to be able to continue operating at almost full capacity for many reaction cycles, leading to favorable economic characteristics. One reason the catalyst may be losing activity in consecutive reactions is due to the proposed reaction process. As the hydrogen gas adsorbs to the platinum particles, it can react with the nearby Ni(OH)₂ and reduce the Ni atoms. This would cause an alloying of Pt and Ni resulting in more effective catalyst activity. While this may increase activity during the reaction, subsequent reactions may be hindered by the altered morphology of the catalyst.

Finally, the overall performance of the 1 wt% Pt-Ni(OH)₂ catalyst was compared to Pt-C and Ni(OH)₂. Figure 8 shows that both the single meal species compounds, Pt-C and Ni(OH)₂), showed little activity with the Ni(OH)₂ showing no activity. The Pt-C reached only 6% hydrazine conversion after 15 minutes whereas the 1 wt% Pt-Ni(OH)₂ reached 100% hydrazine conversion after 15 minutes. These results further confirm that the interaction of the Pt and Ni species on the bimetallic catalyst structure promote beneficial catalyst properties.

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Appendix A. Sample Calculations

Gas Product Amount

Maximum volume of gas possible = mmoles of hydrazine *
$$\left(\frac{22.4 \text{ mL}}{\text{mmol}}\right)$$

22.4 mL = 0.1 mmoles hydrazine * $\left(\frac{22.4 \text{ mL}}{\text{mmol}}\right)$

Hydrazine Conversion

 $Hydrazine\ conversion\ =\ \frac{evolved\ gas}{maximum\ volume\ of\ gas}*100$

 $50\% = \frac{11.2 \, mL}{22.4 \, mL} * \, 100$

Appendix B. Experimental Data

	0 M NaOH	0.5 M NaOH	1 M NaOH	2 M NaOH
time(min)	vol by pass	vol by pass	vol by pass	vol by pass
0	0	0	0	0
1	0.5	0.6	0.7	0.8
2	1	1.1	1.4	2.1
3	1.5	1.7	2.8	3.8
4	1.9	2.8	4.6	6
5	2.2	3.9	6.7	8.3
6	2.4	5.1	8.6	10.3
7	2.5	6.4	10.6	12.4
8	2.6	7.8	12.6	14
9	2.7	9	14.4	15.7
10	2.8	10.1	15.9	17.1
11	2.9	11.2	17.5	18.5
12	3	12.1	18.8	19.3
13	3.1	13	19.8	19.9
14	3.2	14	20.2	20.2
15	3.3	15	20.2	20.2

Solution alkalinity experiments with a NaOH concentration of 0, 0.5, 1, and 2 M.

Temperature experiments at 20 °C, 30 °C, 40 °C, 50 °C, and 60 °C.

	20 C	30 C	40 C	50 C	60 C
time(min)	vol by pass				
0	0	0	0	0	0
1	0.05	0.1	0.4	0.7	1.4
2	0.1	0.2	0.8	1.4	3.2
3	0.15	0.4	1.4	2.8	6
4	0.2	0.6	2.1	4.6	8.6
5	0.25	0.8	3	6.7	11.4
6	0.3	1	3.9	8.6	13.8
7	0.35	1.2	4.7	10.6	16
8	0.4	1.5	5.5	12.6	18
9	0.5	1.8	6.5	14.4	19.5
10	0.6	2.1	7.5	15.9	20.2
11	0.7	2.5	8.5	17.5	
12	0.8	2.9	9.3	18.8	
13	0.9	3.3	10.2	19.8	
14	1	3.7	10.8	20.2	
15	1.1	4.2	11.3	20.2	

Hydrazine concentration experiments with a hydrazine concentration of 0.05, 0.1, 0.2, and 0.3 M.

	0.05 M N2H4	0.1 M N2H4	0.2 M N2H4	0.3 M N2H4
time(min)	vol by pass	vol by pass	vol by pass	vol by pass
0	0	0	0	0
1	0.4	0.7	1	1.3
2	0.8	1.4	2.5	3.2
3	1.6	2.8	5	5.3
4	2.9	4.6	7	7
5	4.2	6.7	8.8	8.7
6	5.7	8.6	10.5	10.3
7	7.2	10.6	12.2	11.3
8	8.6	12.6	13.5	12.4
9	9.6	14.4	14.7	13.4
10	10.1	15.9	15.8	14.3
15	10.1	20.2	20.2	17.8

Selectivity experiment using ammonia trap.

	ammonia trap	no ammonia trap
time(min)	vol by pass	vol by pass
0	0	0
1	0.7	0.7
2	1.4	1.4
3	2.8	2.8
4	4.5	4.6
5	6.8	6.7
6	8.7	8.6
7	10.5	10.6
8	12.5	12.6
9	14.5	14.4
10	15.9	15.9
11	17.4	17.5
12	18.8	18.8
13	19.7	19.8
14	20.2	20.2
15	20.2	20.2

	fresh	2-day	8-day	8-day
time(min)	vol by pass	vol by pass	vol by pass	vol by pass
0	0	0	0	0
1	0.7	0.7	0.7	0.7
2	1.4	1.4	1.4	1.4
3	2.8	2.8	2.5	2.4
4	4.6	4.5	3.9	3.5
5	6.7	6.6	5.3	4.9
6	8.6	8.5	7	6.4
7	10.6	10.5	8.4	7.8
8	12.6	12.5	10	9.5
9	14.4	14.2	11.3	10.8
10	15.9	15.8	12.5	12.2
11	17.5	17.4	13.9	13.5
12	18.8	18.6	15.1	14.5
13	19.8	19.7	16	15.4
14	20.2	20.2	16.8	16.3
15	20.2	20.2	17.3	17.2
16			17.6	17.5
17			17.8	17.8
18			17.9	17.8
19			17.9	17.8
20			17.9	17.8

Stability experiments using fresh, 2 day, and 8 day catalyst.

Cycle 1		Сус	le 2	Cycle 3	
time(min)	vol by pass	time(min)	vol by pass	time(min)	vol by pass
0	0	0	0	0	0
1	0.7	1	1.2	1	0.6
2	1.4	2	2.7	2	1.2
3	2.5	3	3.9	3	1.8
4	4	4	4.8	4	2.3
5	5.8	5	5.9	5	2.8
6	7.8	6	6.8	6	3.4
7	9.9	7	7.7	7	3.9
8	11.8	8	8.5	8	4.4
9	13.5	9	9.4	9	4.9
10	15	10	10.1	10	5.4
11	16.4	11	10.8	11	5.9
12	17.8	12	11.5	12	6.5
13	18.9	13	12.2	13	7
14	19.6	14	13	14	7.5
15	20.2	15	13.9	15	7.9
18	20.2	16	14.5	20	9.8
		17	15.3	25	12
		18	15.9	30	13.9
		19	16.5	35	15.8
		20	17	40	17.3
		21	17.4	45	18.6
		22	17.8	50	19.8
		23	18.2	53	20.2
		24	18.6	55	20.2
		25	19.1		
		26	19.4		
		27	19.8		
		28	20.2		
		31	20.2		

Durability experiments using the same catalyst for three consecutive runs.

Pt-Ni(OH)2		P	Pt-C Ni(OH)2		OH)2
time(min)	vol by pass	time(min)	vol by pass	time(min)	vol by pass
0	0	0	0	0	0
1	0.7	1	0.4	1	0
2	1.4	2	0.7	2	0
3	2.8	3	0.8	3	0
4	4.6	4	1	4	0
5	6.7	5	1.1	5	0
6	8.6	6	1.2	6	0
7	10.6	7	1.2	7	0
8	12.6	8	1.2	8	0
9	14.4	9	1.2	9	0
10	15.9	10	1.2	10	0
11	17.5	15	1.2	15	0
12	18.8				
13	19.8				
14	20.2				
15	20.2				

Catalyst comparison experiments with 1 wt% Pt-Ni(OH)₂, Pt-C, and Ni(OH)₂.