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Non-linear Regression and Simulation of the Effect of Thermal Treatment and Reaction Temperature on Pd-Ni/AC Catalyst for the Thermo Catalytic Decomposition of Methane

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Abstract: The effects of the thermal treatment and reaction temperatures on 5% (wt/wt) 1:1 (mol:mol) *Pd-Ni* on activated carbon (AC-ITDI) catalyst acquired from the Industrial Technology Development Institute (ITDI) of the Department of Science and Technology (DOST) of the Philippines (*Pd-Ni*/AC) for the thermocatalytic decomposition of CH_4 were determined in this study. The thermal treatment parameters investigated were the carbonization temperature and calcination temperature; the effect of reduction temperature was not investigated. AC carbonization was done at 700°C, 800°C and 900°C in argon and catalyst calcination was done at 500°C, 600°C and 800°C. The thermal decomposition reaction temperatures were 750°C, 850°C and 950°C for the catalyst that exhibited the best initial activity. Catalyst pre-characterization showed that the catalyst pore size increased with carbonization temperature but decreased with calcination temperature. Pd particle dispersion was better also at lower calcination temperatures. Catalytic activity test results show that *Pd-Ni*/AC carbonized at 700°C and calcined at 500°C had the highest initial H_2 yield (0.4056 mol H_2/mol CH_4), an H_2 yield of (0.0276 mol H_2/mol CH_4) after 24 hours and a 7-hour average H_2 yield of 0.007371. The developed non-linear regression model indicated that H_2 yield is mainly affected by carbonization temperature with a total parameter significance value of 94.5776% due to its effect on catalyst pore size and by calcination temperature with a parameter significance value of 5.4224% due to its effect on *Pd* particle dispersion. The predicted maximum H_2 yield value of 0.00689 was found at a carbonization temperature of 900°C and a calcination temperature of 600°C. H_2 yield values are expected to increase at higher reaction temperatures (>950°C).

Key Words: activated carbon (ITDI), methane decomposition, non-linear regression, simulation, thermal treatment

1. INTRODUCTION

Carbon-based catalysts have been of interest for thermocatalytic decomposition of methane since these show several advantages over metal catalysts (Muradov et al. 2005; Bai et al. 2005; Lee et al. 2008). Catalysts with activated carbon (AC) as a support material exhibited high initial catalytic activity but then its activity decreased significantly with time due to carbon deposition over the external surface of the catalyst particles.

When AC and metal particles are combined in a catalyst, valuable filamentous carbons and hydrogen can be produced from methane decomposition. *Ni* loaded on AC showed higher activity in methane decomposition than AC alone (Bai et al. 2007). It was reported that if *Ni* metal was modified with other metals, it was expected that the balance of deposition and diffusion rates of carbons would be changed which can improve the catalytic performance of the supported *Ni* catalyst (Takenaka et al. 2003; Ogihara et al. 2006; Reshetenko et al. 2003).

No study has yet been done on the use of thermally-treated AC-based catalysts. Thus, in this study the use of *Pd-Ni*/AC supported on thermally-treated ITDI AC for thermocatalytic decomposition of CH_4 was investigated. The ITDI AC was produced from coconut shells which are abundant in the Philippines and Vietnam.

2. METHODOLOGY

2.1 Catalyst Preparation

AC from ITDI was dried for 24h at 110°C and then carbonized at different temperatures: 700°C, 800°C and 900°C. *Pd* and *Ni* were impregnated on AC by wet impregnation method. Calcination was done at 500°C for 5 hours. Catalyst reduction was done with 40ml/min of H_2 at 300°C for an hour. After the reduction process, H_2 was flushed out with *Ar* at 650°C for 2.0 hours.

2.2 Experimental Set –up

The experimental set-up consisted of a U-tube quartz reactor, an electric furnace, thermocouple, temperature controller unit, a four-way valve, flow meters, and a computer with Chromatographic Station for Window (CSW) as shown in Figure 1.

Activity tests were done in a U-tube 7-mm I.D. quartz reactor loaded with 0.2 g of catalyst. Reactions were done at 650°C with atmospheric pressure using 20/80 mL/min CH_4/He. The catalyst which exhibited the highest average H_2 yield was then subjected to further catalytic activity testing at different reaction temperatures of 750°C, 850°C and 950°C. The exit gas composition was determined using gas chromatography. The data analysed were from the first seven hours of catalytic activity testing.

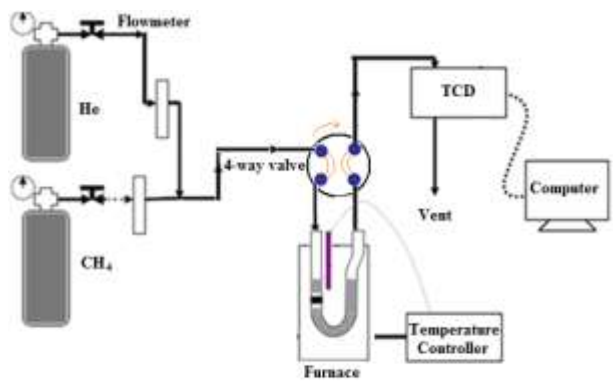

Figure 1. Thermocatalytic Decomposition of Methane Laboratory Set-Up

The following equation was used to determine the H_2 Yield:

$$Y_{H_2} = \frac{[H_2]_f}{[CH_4]_i} \qquad \text{(Eq. 1)}$$

where:

$[CH_4]$ = concentration of $CH_4(g)$;
$[H_2]$ = concentration of $H_2(g)$;

i,f = subscripts designating initial and final conditions, respectively;
Y_{H2} = H_2 *Yield.*

The determination of the significance and the optimization of the thermal treatment parameters based on maximum Y_{H2} were done using multiple non-linear regressions through the Solver® function of Microsoft® Excel® 2010 with a minimum of five Generalized Reduced Gradient (GRG) nonlinear iterations. Taking a preliminary assumption that there is no interaction between the calcination temperature and the carbonization temperature, the general non-linear characteristic equation used takes a summative form as follows:

$$Y_{H_2} = \sum_{i=1}^{3}\sum_{j=1}^{2} s_{iP_j} C_{iP_j} P_{ij}^{\ i} \qquad \text{(Eq. 2)}$$

where:
i = dummy variable taking integer values;
C = coefficient corresponding to parameter, *P*
P = parameter criterion corresponding to:
P_{i1} = carbonization temperature;
P_{i2} = calcination temperature;

3. RESULTS AND DISCUSSIONS

3.1 *Effect of Thermal treatment on H_2 Yield of Pd-Ni/AC700*

The H_2 yield for the catalysts treated at different treatment temperatures are shown in Table 1.

Table 1. Summary of Activity Test Results

Run	P_{i1} °C	P_{i2} °C	$Y\ H_2$
1	700	500	0.007371
2	800	800	0.004300
3	900	600	0.006107
4	700	600	0.006457
5	800	500	0.005414
6	900	800	0.005650
7	700	800	0.003957
8	800	600	0.005879
9	900	500	0.005300

In order to determine the relative effect of each of the treatment processes, the temperature values were translated to integer values as shown in Table 2.

Table 2. Translated Summary of Activity Test Results

Run	P_{i1} °C	P_{i2} °C	$Y\ H_2$
1	1	1	0.007371
2	2	3	0.004300
3	3	2	0.006107
4	1	2	0.006457
5	2	1	0.005414
6	3	3	0.005650
7	1	3	0.003957
8	2	2	0.005879
9	3	1	0.005300

Defining the parameter significance as the relative value of the coefficient of the parameter compared to the sum of the total values of the coefficients, as in Eq. 3, the summary of the GRG nonlinear regression results with the relative parameter significance is shown in Table 3.

$$S_{iP_j} = \frac{F_{iP_j}}{\sum F} \qquad \text{(Eq. 3)}$$

Table 3. Summary of GRG Nonlinear Multiple Regression Results

Thermal Treatment Parameter		**Parameter Coefficient (F_{iPj})**	**Parameter Significance (S)**
Carbonization Temperature	P_{11}	9.74E-05	0.0046%
	P_{21}	1.008908	47.3555%
	P_{31}	1.005968	47.2175%
Calcination Temperature	P_{12}	0.007079	0.3323%
	P_{22}	-0.00189	0.0887%
	P_{32}	-0.10656	5.0014%

The regression data in Table 3 show that the most significant parameters are the second-order and third-order carbonization temperatures both at 47%, followed by the third-order calcination temperature at 5%. Since the parameter values for the carbonization temperature are positive, these values mean that, for *Pd-Ni*/AC catalysts, the H_2 yield increased non-linearly with increasing carbonization temperature. On the other hand, since the parameter value for the third-order calcination temperature is negative, this means that the H_2 yield decreased non-linearly with increasing calcination temperature. However, the parameter significance of third order calcination temperature of only 5% implies that H_2 Yield is not a strong function of third order calcination temperature.

These results agree with the findings from a separate study (Dao, 2011), where there was an observed increase in pore size with increasing carbonization temperature and decreasing calcination temperature. Also, it was found that there was higher Pd dispersion over the AC support material at lower calcination temperatures. Those results show that the dependence of H_2 yield on the thermal treatment processes was mainly due to the changes in the pore size and the *Pd* particle dispersion over the support material of the catalyst. More specifically, H_2 yield increases with increasing pore size and Pd particle dispersion.

Simulating the model in Eq.2 using the determined regression parameters in Table 3 shows that a *predicted* maximum H_2 yield of 0.00689 at a carbonization temperature of 900°C and a calcination temperature of 600°C. The predicted maximum deviates from the experimental maximum of 0.007371 by 6.5%, while the over-all RMS of the developed model is 8.13 x 10^{-7} which implies its accuracy and reliability.

3.2 *Effect of Reaction Temperature on H_2 Yield of Pd-Ni/AC700*

Based on the values in Tables 1 and 2, it can be seen that the highest H_2 yield of 0.007371 was produced by the *Pd-Ni*/AC catalyst carbonized at 700°C and calcined at 500°C. While the expected lowest value of the calcination temperature agrees with the regression results, the lowest value for the carbonization temperature does not seem to agree with the regression results. This discrepancy suggests an interaction to be present between the carbonization and calcination temperatures, and further investigation on this interaction might be necessary.

Hence, the catalyst carbonized at 700°C and calcined at 500°C was subjected to further activity testing at different reaction temperatures. The results of the activity tests are shown in Figure 2.

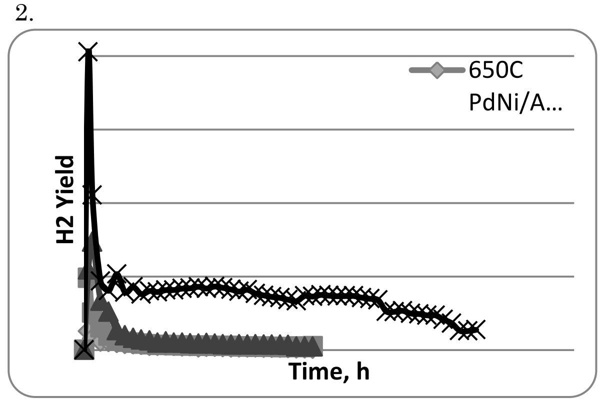

Figure 2. H_2 Yield at Different Reaction Temperatures (Pd-Ni/AC700)

It can be seen that the H_2 yield increased with reaction temperature (650-950°C), especially with an increase to 950°C. The maximum H_2 yield of catalyst at reaction of 950°C was 0.456. Time-course activity test results show that for all temperatures there was a rapid decrease in yield, followed by a more stable catalytic activity. Compared to the other reaction temperatures, the reaction held at 950°C showed the least resistance to deactivation, as exhibited by its higher yield throughout the activity test. This behaviour is supported in literature (Takenaka et al. 2003) where the catalytic activity increased with increasing reaction temperature. In this study, the total metal loading was only 5% (w/w) but it was still active at 950°C.

4. CONCLUSIONS

The effect of thermal treatment temperature on the activity of *Pd-Ni*/AC catalyst prepared by wet impregnation with a total metal loading of 5% (w/w) and *Ni:Pd* mole ratio of 1:1 for the thermocatalytic decomposition of CH_4 was investigated. The various carbonization temperatures were 700, 800, 900°C and the calcination temperatures were 500, 600, 800°C. A multiple non-linear regression model was successfully developed, and the results show that higher H_2 yields are expected are higher carbonization temperatures due to increasing catalyst pore size and lower calcination temperatures due to better *Pd* particle dispersion.

The effect of reaction temperature was investigated with *Pd-Ni*/AC700_500 catalyst which had the highest initial H_2 yield. Graphical analysis shows that higher H_2 yields are expected at higher reaction temperatures. The regression model, however, did not consider the possibility of sintering and catalyst deactivation at even higher reaction temperatures.

5. ACKNOWLEDGMENTS

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