

Catalytic Hydrogen Generation from Hydrazine Hydrate for Fuel Cell Application

Young Bae Jang, Tak Hee Kim, Min Ho Sun, Jun Lee, Sung June Cho[†]

Department of Applied Chemical Engineering, Center for Functional Nano Fine Chemicals (BK21 Program), Chonnam National University, Gwangju 500-757, Korea

ABSTRACT: Hydrazine hydrate has been important class of chemicals as foaming agent, anticorrosion agent, synthetic resin, rubber, agricultural chemicals etc. It also contains a lot of hydrogen ranging from 4.4 to 8.0 Hwt%, depending on its purity. Hydrogen can be released or generated through the catalytic reaction with iridium metal catalyst that has been employed for the thruster propulsion in manoeuvring of the satellite.

In this work, the catalyst has been developed and characterized with X-ray diffraction, transmission electron microscopy, atomic force microscopy, extended X-ray absorption fine structure and etc. The obtained granule catalyst was highly active for the decomposition of hydrazine hydrate, thus generating hydrogen at high turnover rate. The catalytic reactor equipped with the honeycomb catalyst containing iridium catalyst also showed the sustainable activity for the hydrogen generation when the liquid hydrazine hydrate was injected in pulse mode.

Keywords: hydrogen generation, hydrazine hydrate, iridium catalyst, honeycomb

1. INTRODUCTION

Hydrogen energy technology has been investigated extensively because of clean and sustainable energy alternative to fossil fuel. Infrastructure for hydrogen energy utilization includes production, storage and transport to the site where hydrogen energy is consumed. Still most of hydrogen production relies on the conversion of fossil fuel into hydrogen using catalytic process.[1]

There are also numerous developments in hydrogen storage technology, mostly the material based. Metal complex hydride, carbon nanotube, metal organic framework etc. have thus been studied worldwide.[2] However, none of the developing technologies does not satisfy the requirement for the hydrogen energy storage,

safety and storage/retrieval efficiency, respectively.

Hydrazine, N₂H₄, as monopropellant was investigated for use in satellite propulsion using an Ir based catalyst.[3] Hydrazine can be converted in the following two ways: N₂H₄(g) → N₂(g)+2H₂(g), ΔH = -95.4 kJ mol⁻¹ and 3N₂H₄(g) → 4NH₃+N₂(g), ΔH = -157 kJ mol⁻¹. [4] However, the toxicity and the explosive character of anhydrous hydrazine has been an obstacle for the utilization of hydrazine as hydrogen carrier. Recently, the hydrazine hydrate was utilized as hydrogen carrier in the fuel power generation that the anion exchanged membrane was employed.[5] In fact, the dangerous property can be removed readily when anhydrous hydrazine is combined with water while the content of hydrogen in

hydrazine hydrate can be controlled to 4.4 to 8.0 Hwt% depending on the water content.

In the mean time, the catalytic performance over the decomposition of hydrazine hydrate is still under the investigation. The structural property of the Ir catalyst was studied extensively due to the importance of the unique catalytic activity for NH_3 and N_2H_4 decomposition for the hydrogen generation free of CO_x . [6] The Ir nanoparticle can be prepared on zeolite [7] and $\gamma\text{-Al}_2\text{O}_3$ support [8,9] using ion exchange, incipient wetness, chemical vapor deposition etc. The atomic structure of such nanoparticle in the supercage of the NaY zeolite and on the $\gamma\text{-Al}_2\text{O}_3$ was confirmed by XAFS. The small Ir_4 cluster was derived when the $\text{Ir}_4(\text{CO})_{12}$ complex was decarbonylated on the support.

Recently, we reported the preparation of 30 wt% Ir catalyst supported on $\gamma\text{-Al}_2\text{O}_3$ using dry-soak method similar to the multiple impregnations. [10] The results from the X-ray diffraction, transmission electron microscopy, hydrogen chemisorption and X-ray absorption fine structure analysis suggested the formation of Ir nanoparticle covered with oxygen. The particle size was limited to less than 2 nm though the loading was extremely high near 30 wt%.

In this work, a series of Ir catalyst was prepared to have 5 – 20 wt% metal content using dry-soak method since the lower metal content is preferred for the commercial catalytic application such as hydrogen generation. The atomic and textural properties of Ir catalyst were probed with transmission electron microscopy, atomic force microscopy and X-ray absorption fine structure. Also, the catalytic performance of the honeycomb type catalyst was obtained using the pulse mode reaction.

2. EXPERIMENTAL

The powder type catalyst was prepared and characterized following the procedure reported earlier. [10] The nominal metal

loading was controlled to 5, 10 and 20 wt%, respectively.

For the preparation of the honeycomb type catalyst, the honeycomb obtained from DongSuh Ceracomb was coated with 10wt% alumina and calcined to form the strongly binding between the substrate and alumina. The alumina coated honeycomb was impregnated with IrCl_3 (51wt%, Johnson Matthey) up to 2 wt% Ir content with respect to total weight that was corresponded to 21.1 wt% with respect to the coated alumina. The catalyst was calcined at 773 K and reduced with flowing hydrogen at 573 K in order to get the reduced catalyst.

For the catalytic reaction test, hydrazine hydrate from Daejung was analyzed using GC to determine the % level of hydrazine. The obtained value was 55.1 wt% corresponding to 6.8 Hwt%. The hydrazine was injected in pulse mode over the three staged honeycomb catalysts with 10 mm thickness. The typical pulse mode was 50 msec injection and 5 sec off. Just after the reaction, the product gas was passed through the water trap. The NH_3 concentration in the effluent gas was monitored *on line* using Eco Physics CLS 844 CM hr instrument. The overall flow was measured using wet gas meter to obtain the volume of the decomposed gas. Fig. 1 shows the reaction system for hydrazine decomposition.

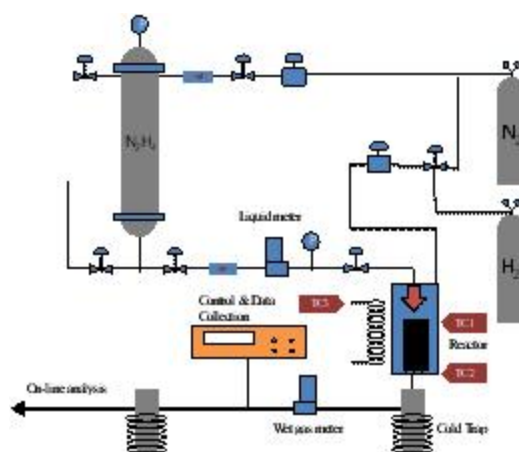


Figure 1: Reaction system for hydrazine decomposition

3. RESULTS AND DISCUSSION

Table I shows the summary of the characterization of the Ir catalyst in powder type. The particle was found to be 1.3-1.5 referred from the results of hydrogen chemisorptions. The high resolution TEM images also shows the same particle size as shown in Fig. 2. The particle size of Ir catalyst in the present work was much smaller than the reported one. [10]

Table I: Surface properties of the Ir catalyst measured by BET adsorption method, hydrogen adsorption measurement and X-ray photoelectron spectroscopy.

Sample	IrAl-5	IrAl-10	IrAl-20
Loading (wt%) ¹	5.8	9.8	16.4
BET surface area (m ² g ⁻¹)	112	129	130
Pore volume (ccg ⁻¹)	0.33	0.35	0.31
H adsorption (μmol g ⁻¹)	227	390	557
Dispersion (%) ²	75	77	65
Particle size (nm) ³	1.3	1.3	1.5

¹Elemental analysis by X-ray photoelectron spectroscopy

²Assuming the adsorption stoichiometry is one hydrogen per Pt atom

³Assuming spherical particle, d (nm)=100/Dispersion(%)

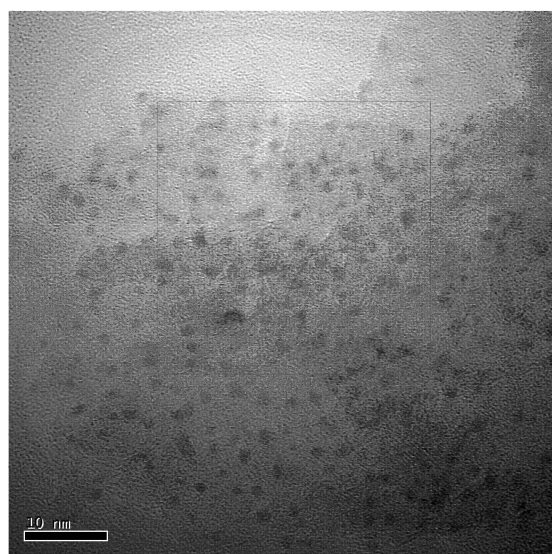


Figure 2: HRTEM photograph of IrAl-10.

The textural properties of the Ir catalyst were also reflected in the AFM image. At 5.9 wt% loading, the very rough surface was obtained, partly consistent with the formation of 1-2 nm sized nanoparticles. Increasing the metal content, the texture of the surface became smooth probably due to that the number density of the particle over the catalyst surface was so high that the AFM tip can detect only the Ir metal. A series of the AFM image as a function metal content suggested that the catalyst surface was covered fully with the Ir nanoparticles and it became smooth.

Table II: Structural parameters obtained from EXAFS curve fitting for the Ir catalyst*

sample	pair	N^a	R (nm) ^b	σ^2 (pm ²) ^c
IrAl-5	Ir-O	2.9	0.202	72
	Ir-Al	1.1	0.245	46
	Ir-Ir	1.6	0.267	53
IrAl-10	Ir-O	2.9	0.202	77
	Ir-Al	1.0	0.251	37
	Ir-Ir	3.5	0.268	65
IrAl-20	Ir-O	2.1	0.196	71
	Ir-Ir	7.7	0.269	80

*Number of independent free parameters, N_{idp} and variable, N_{var} in the fit were 10 and 6, respectively, which was given

by $N_{idp} = \frac{2\Delta k \cdot \Delta r}{\pi} + 2$ where Δk and Δr were 100 nm⁻¹ (30-

130 nm⁻¹) and 0.159 nm (0.149-0.308 nm, respectively).

^aCoordination number (± 0.5), ^bBond distance (± 0.001 nm),

^cthe Debye-Waller factor.

The XAFS data was analyzed using the UWXAFS2 program.[11-13] The obtained structural parameters are listed in Table II. Three atomic pair distribution functions for low loading Ir catalyst were obtained, an Ir-Ir pair at 0.27 nm, an Ir-Al pair at 0.25 nm and an Ir-O pair at 0.20 nm. The detection of the Ir-Al pair distribution indicated the strong metal-support interaction. The Ir-Al pair distribution became disappeared with

the increase of the metal content systematically again. The Ir-Ir pair distribution increased from 1.6 to 7.7 with the increase of the metal content, which consistent with the particle shape and the textural properties obtained from the TEM observation and the AFM measurement. Further the structure contained the Ir-Ir distance, which is different from those in IrO₂, 0.315 nm and 0.355 nm. Rather, it was very similar to that of Ir metal, indicating an Ir metal structure surrounded by oxygen.

The Ir-O distribution was decreased slightly from 2.9 to 2.1. Such small Ir-O coordination suggested the presence of the adsorbed oxygen. From the coordination number, it seemed that the structure of Ir nanoparticle was the Ir metal core covered with oxygen.

Electronic structure of the Ir nanoparticle was probed with X-ray photoelectron spectroscopy. The binding energy of Ir4f_{5/2} and Ir4f_{7/2} was shifted to higher energy referenced to that of the O1s in Al₂O₃. This was consistent with the partially oxidized Ir nanoparticle since the reduced Ir metal core was covered with the adsorbed oxygen. Therefore, the results from XPS was consistent with the results of TEM, AFM and EXAFS.

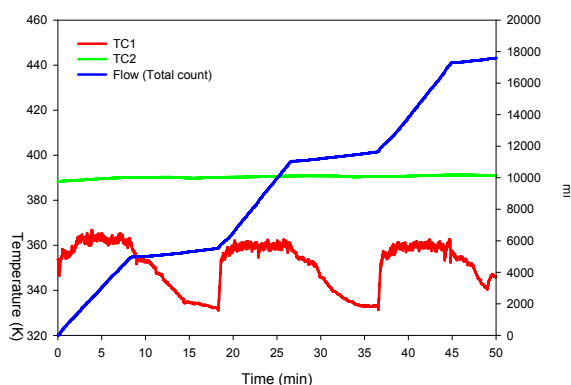


Figure 3: Quantity of gas production and change of temperature with time on stream in pulse mode.

Fig. 3 shows the results of hydrazine decomposition with time on stream. The

furnace temperature was set to 473 K. The TC1 and TC2 indicated the temperature for the inlet and outlet of the three staged honeycomb, respectively.

Upon the injection of hydrazine hydrate, the decomposition reaction proceeded readily even at 330 K. The temperature was raised to 360 K with the sequential pulse mode for 30 min in total. The gas evolution was reached to 5.3 l and the catalytic reactivity was maintained during the reaction. Further, there was no formation of NH₃, referred from the *on-line* gas monitor. Therefore, the decomposition reaction of hydrazine hydrate over the catalyst proceeded readily without deterioration of the activity and also the formation of NH₃, which highlighted hydrazine hydrate as the potential hydrogen carrier.

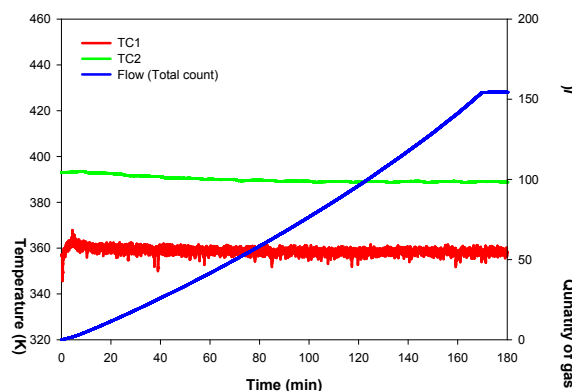


Figure 4: Quantity of gas production and change of temperature with time on stream in continuous pulse mode for 3 hrs.

The continuous pulse reaction was performed over the same catalyst after the simple regeneration at 474 K to remove the water. The water in hydrazine hydrate was remained on the surface of the catalyst so as to decrease the decomposition activity. Thus, the reaction was performed maintaining the outlet temperature, TC2 above 370 K. The results of reaction in Fig. 4 show that the catalytic activity of the honeycomb catalyst was the same during the continuous reaction. The temperature at the inlet and outlet of the catalyst were maintained and also the quantity of gas

evolution increased linearly, indicating there is no decrease of the catalytic activity. However, the decomposition reaction was finished due to the water trap was filled fully. This caused the wetting of the catalyst, resulting in the abrupt decrease of the catalytic activity.

4. CONCLUSION

Hydrazine hydrate has been investigated as potential hydrogen energy carrier in the present work. The obtained Ir particle size was ranged from 1.3 to 1.9 nm with the increase of the metal loading to ~ 16 wt%. The honeycomb catalyst with similar metal loading with respect to alumina contained sustainable catalytic activity without significant loss of catalytic activity for the continuous pulse reaction mode during more than 160 min. Therefore, it was believed that the decomposition of hydrazine hydrate can be potential hydrogen generation reaction for fuel cell.

ACKNOWLEDGEMENT

This work was supported by the Hydrogen Energy R & D Center, one of the 21st Century Frontier R & D Programs, funded by the Ministry of Science and Technology, Korea.

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