Development of Novel Dehydrogenation Catalyst for Hydrogen Carrier System

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Abstract: Chiyoda Corporation developed "SPERA Hydrogen^{TM}" system for the massive H_2 storage and transportation technology through a pilot plant demonstration. The system employs the Organic Chemical Hydride method (OCH method). In the method, hydrogen is fixed to toluene and converted to methylcyclohexane (MCH) as a Liquid Organic Hydrogen Carrier (LOHC). Since hydrogen is stored in the MCH molecule, hydrogen is able to be stored and transported under the ambient temperature and pressure in the liquid state. Hydrogen gas volume is reduced around bellower than 1/500. If we reduce the volume physically, we need more than 50MPa, it is realized under the ambient condition by using chemical reaction in this method. The key technology of "SPERA Hydrogen^{TM}" system was a development of a novel dehydrogenation catalyst which is needed for hydrogen generation after transportation at the hydrogen utilization place, since there was not catalyst with stable performance for MCH dehydrogenation due to severe coking for the catalyst deactivation. The developed novel dehydrogenation catalyst is nano-platinum particle on the alumina carrier in a uniform type. In this paper, we introduce the development of the dehydrogenation catalyst, outline of "SPERA Hydrogen^{TM}" system and future prospect for hydrogen utilization in each sector including CCU (Carbon Dioxide Capture and utilization).

Keywords: nano-platinum catalyst, Dehydrogenation, Hydrogen, Storage, Transportation.

1. Introduction

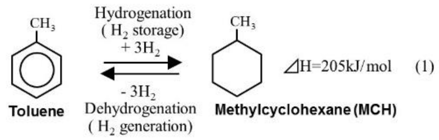
We are facing to the climate change issue by carbon emission, we have to promote a decarbonization of energy system. Hydrogen energy has much potential for a solution of the issue. Japanese government issued Strategic Road Map of Hydrogen and Fuel Call in 2014[1)], and it was revised in 2016. In addition, Basic Hydrogen Strategy also issued in last December[2)]. The 5th Basic Energy Plan of Japan will be issued in this summer[3)], the Hydrogen energy will be mentioned in it based on the Basic Hydrogen Strategy. The Ministerial Meeting on Hydrogen Energy will be held in Japan in this year on 23rd Oct. [4)]

Since the massive hydrogen storage and transportation technology is needed for hydrogen energy system, brisk R&D for hydrogen energy carrier is promoted in these years. Chiyoda Corporation has been completed a technical development of "SPERA Hydrogen^{TM}" system for the massive H_2 storage and transportation technology through a pilot plant demonstration. The system employs the Organic Chemical Hydride method (OCH method). In the method, hydrogen is fixed to toluene and converted to methylcyclohexane (MCH) as a Liquid Organic Hydrogen Carrier (LOHC). Toluene and MCH are gasoline components and in the liquid phase under the ambient temperature and pressure. In the method, the potential risk for the massive hydrogen storage and transportation can be reduced to the conventional one for the gasoline storage and transportation, since hydrogen is stored as MCH in the liquid phase under the ambient condition as same as gasoline. It is considered that the conventional storage tanks and the chemical tankers which are conventional infrastructure can be used to this system is also the merit. We named the developed system "SPERA Hydrogen^{TM}" system. The key technology of "SPERA Hydrogen^{TM}" system was a novel dehydrogenation catalyst development. The dehydrogenation catalyst is nano-platinum particle on alumina carrier in a uniform type. In this paper, we introduce the development of the dehydrogenation catalyst and "SPERA Hydrogen^{TM}" system.

2. SPERA Hydrogen System

2-1. Dehydrogenation Catalyst

We employs Toluene/Methylcyclohexane (MCH) system as the LOHC. Equation (1) shows the hydrogenation (H_2 storage reaction) and dehydrogenation (H_2 generation reaction).



The method had been investigated in the Euro-Quebec project as the third candidate with liquefied hydrogen and liquefied ammonia method in 1980's. In those days, the dehydrogenation catalyst life was only 1or 2 days due to sever coking. Chiyoda started the catalyst development since 2002, and completed the catalyst development including industrial production of the catalyst in 2011.

Fig.1 shows the estimated surface model of the developed dehydrogenation catalyst[5]. The catalyst is partially sulfided nano-sized Pt cluster on the Al_2O_3 catalyst. The catalyst has very high performance more than 10,000hrs catalyst life with more than 95% of MCH conversion and more than 99% of toluene selectivity in the MCH dehydrogenation reaction in the laboratory test. The nano-sized Pt cluster has dramatically improved the activity and catalytic life. The role of sulfur is considered to prevent the decomposition of MCH on the Pt cluster. Fig.2 shows the results of the measurement for the dispersion of sulfur and platinum atoms in the catalyst with EPMA (Electron Probe Micro Analyzer). The developed catalyst has a uniform dispersion of sulfur and Platinum atoms.

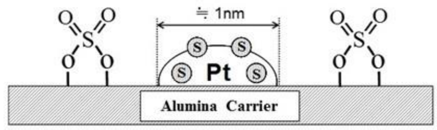


Fig.1 Estimated surface model of dehydrogenation catalyst

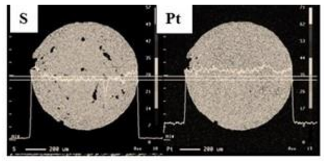


Fig.2 Result of S and Pt dispersion measurement by EPMA

2-2. Technical demonstration

Fig.3 shows the pilot plant for the technical demonstration with 50Nm^3-H_2/h capasity[6]. In the demonstration, both of hydrogenation and dehydro genation were operated at the same location. The operastion was started in Apr. 2013, and completed in Nov. 2014 with highly stable performance for around totally 10,000hrs. Since the heat exchanger type reactor are employed for the both reaction, the scale up is relatively easy.

Fig.4 shows the reaction results of hydrogenation and dehydrogenation. In the initial period, it was operated at the several conditions to get the parameters for a development of the simulator. The reaction pressure is lower than 1MPa in the both reaction.

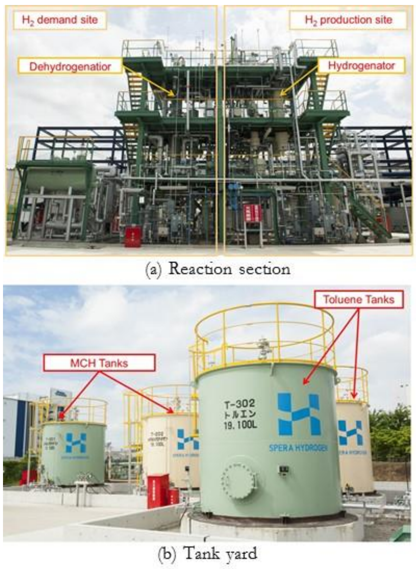


Figure 3 Pilot plant for "SPERA Hydrogen" System

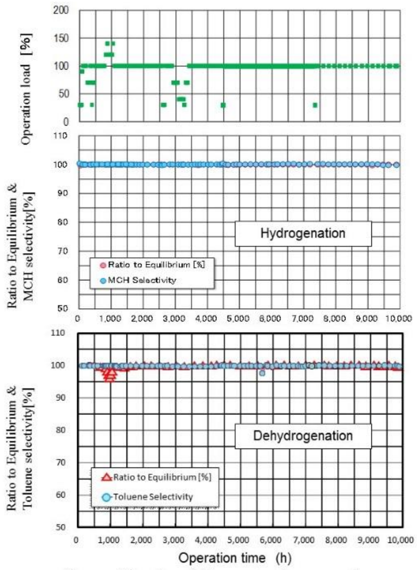


Figure 4 Results of demonstration operation

The hydrogenation temperature is lower than 250 ℃ and the dehydrogenation temperature is lower than 400 ℃. In the Fig.4, the both conversions are shown in the ratio to the equiliblium conversion. The results of the both reaction shows the well stable performance. The hydrogenation process performance is toluene conversion: >99%, MCH selectivity: >99%, MCH yield: >99%. The dehydrogenation process performance is MCH conversion: >95%, toluene selectivity: >99%, hydrogen and toluene yield: >95%. If the dehydrogenation conversion declined to 95%, catalyst will be exchanged and Pt on the catalyst will be recovered from the spent catalyst for the flesh catalyst preparation[7,8].

Now, we are executing the first international hydrogen supply chain demonstration project for hydrogen transportation from Brunei Darussalam in South East Asia to Kawasaki City in Japan in 2020 as a member of AHEAD (Advanced Hydrogen Energy Chain Association for Technology Development)[9]. AHEAD is organized by Chiyoda Corporation, Mitsubishi Corporation, Mitsui Co& Ltd. and Nippon Yusen (NYK) and it is founded by NEDO (New Energy and Industrial Technology Development Organization) which is governmental organization.

3. Prospects for Hydrogen Utilization

Figure 5 shows the future prospects for hydrogen utilization in each sector. Fuel cell vehicle (FCV) and residential fuel cell are already commercialized. It is highly effective to reduce CO_2 emission from car or family house which are small and decentralized CO_2 emission resources. It is necessary to reduce the CO_2 emission from large emission sources such as power generation, City gas and industrial sectors.

Since the power generation sector is the biggest emission source, we need to utilize hydrogen as generation fuel. There two ways for it. One is hydrogen will be used for the thermal power generation, the other is fuel for fuel cells as the decentralized power generation. The several MW class fuel Cells are viable for the airport, station or city hall which should be worked under the blackout due to the earth quake etc. In the city gas sector, hydrogen will be mixed to natural gas as Hydrogen methane which is called Hytan in the first step, and final way is considered that hydrogen produced from renewable energy and recovered CO_2 from large emission source are react to CO and H_2O through the reverse shift reaction, and then CO and H_2 are reacted to CH_4 through the sabatier reaction. In the industrial sector, recovered CO_2 will be sequestrated as CCS (Carbon dioxide Capture and Sequestration) or renewable hydrogen will be react recovered CO_2 as CCU (Carbon dioxide Capture and Utilization).

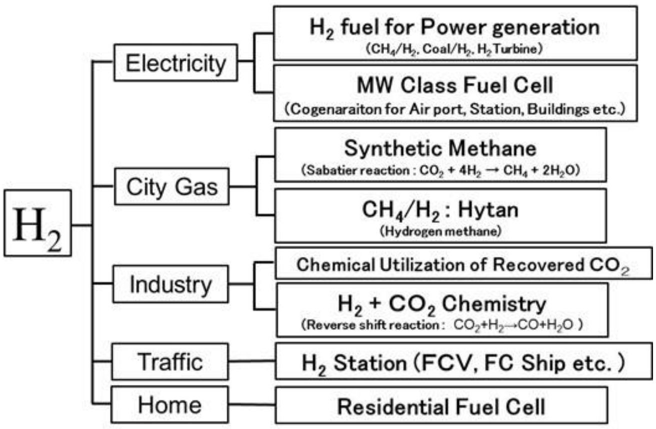


Figure 5 Prospects for Hydrogen Utilization

CCS and CCU will be significant way as physical and chemical carbon reduction in the future. In addition, NH_3 from renewable hydrogen will be viable for CCU as recovered CO_2 and NH_3 are react to $(NH_2)_2CO$ which is fertilizer[10]. This concept means emitted CO_2 from industry is go back to the natural carbon cycle by using N_2 as intermediate. Since the present NH_3 is produced from natural gas, NH_3 from renewable energy is also significant for the food issue by increasing population and gas depletion in the future.

4. Acknowledgement

The first international hydrogen supply chain demonstration project by AHEAD is supported by NEDO. We express words of gratitude to NEDO.

5. Conclusion

Chiyoda completed the technical demonstration through the pilot plant demonstration. Now, we are executing the first international hydrogen supply chain demonstration project as a member of AHEAD. We would like to contribute to establishment of low carbon sosiety, through the promotion of the hydrogen energy systems and reduction of CO_2 emission to prevent the global warming issue with the commercialization of “SPERA Hydrogen” system.

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