Development of large-scale H_2 storage and transportation technology with Liquid Organic Hydrogen Carrier (LOHC)

Yoshimi Okada[1], Mitsunori Shimura[2]

Principal researcher, Technology Development Unit, Chiyoda Corporation
Deputy General Manager, Technology Development Unit, Chiyoda Corporation

4-6-2, Minatomirai, Nishi-ku, Yokohama 220-8765 Yokohama, Japan
yookada@ykh.chiyoda.co.jp, mshimura@ykh.chiyoda.jp

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Abstract

Chiyoda Corporation has been proposed the global hydrogen supply chain concept by liquid organic hydrogen carrier (LOHC) with Toluene/Methylcyclohexane system. In this method, hydrogen is fixed to toluene (C_7H_8) with the hydrogenation reaction and converted into methylcyclohaxane (MCH: C_7H_{14}) that is able to be transported with a chemical tanker as same as toluene. In the demand site, hydrogen is generated from MCH by dehydrogenation reaction, and toluene is recovered for the recycle use. LOHC is suitable for large-scale storage and long distance transportation due to the ambient condition with the low potential risk.

Keywords

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1. Introduction

Renewable energy is expected to be an alternative energy as post-fossil resources. Hydrogen is a clean energy carrier since it is converted to water after utilization, and hydrogen can be produced from any primary energies including renewable energy. It is considered that hydrogen energy can be converted from renewable energy including solar energy in the future. Hydrogen produced from water by renewable energy can be a final energy system as “solar and water energy system”.
Photovoltaic (PV), concentration solar power (CSP) and concentration solar thermal systems utilize solar energy directly as renewable energy. Hydrogen production from water by electrolysis is an effective method for conversion of the electricity from

renewable energy to hydrogen energy. We considered that Photo-catalytic water production will be commercialized which is direct conversion of solar energy to hydrogen energy in addition to the direct utilization of solar energy in the future.

While hydrogen storage and transportation technologies are commercialized by compressed hydrogen method for fuel cell vehicles (FCV) and liquefied hydrogen method for the hydrogen fuelling stations in a small-scale, the technology for a large-scale storage and transportation has not been commercialized. Chiyoda Corporation has been developed the organic chemical hydride (OCH) method using a liquid organic hydrogen carrier (LOHC) as the suitable method for a large-scale storage and transportation of hydrogen energy, it is under demonstration step. In this paper, OCH method and development status are introduced.

2. Hydrogen supply chain

Fig.1 shows the hydrogen supply chain concept which is proposed since 2004in Japan, by using hydrogen storage and transportation system by OCH method[1-6]. Japan has been faced to the issues of CO_2 emission and future fossil energy drain. In addition, Importance of renewable energy utilization has been recognized after Fukushima nuclear power plant accident by tsunami disaster in 2011 in Japan. However, Japan does not have much renewable energy as same as fossil energy.

The hydrogen supply chain concept is consists of two steps. In the first step, Hydrogen as clean hydrogen from fossil resources is utilized with carbon dioxide capture and storage (CCS), enhanced oil recovery (EOR) or Enhanced coal bed methane (ECBM). At present, CO_2 is the only waste at present as Greenhouse gas, but in the future, CO_2 will be the precious carbon resources. Because H_2 can be produced from water by renewable energy in the future, but carbon resources will not to be prepared easily. Carbon exists as CO_2 in the air at only around 400ppm, other carbon atoms exist in the plants, animals, fishes or human beings as in the life except hydrocarbons as fossil resources. Such like carbons are difficult to be utilized as carbon resources. CO_2 reservation as the results of CCS or EOR can be future precious carbon resources, because H_2 from renewable energy and carbon from CO_2 reservation will be able to produce chemicals or fuels by chemical reaction of H_2 and CO_2 which is called as reverse shift reaction.

In the second step, hydrogen from renewable energy which is called green hydrogen will be utilized. In the hydrogen supply chain concept, it will not to be needed to change the infrastructures in the first step to the enlargement of renewable energy according to ages.

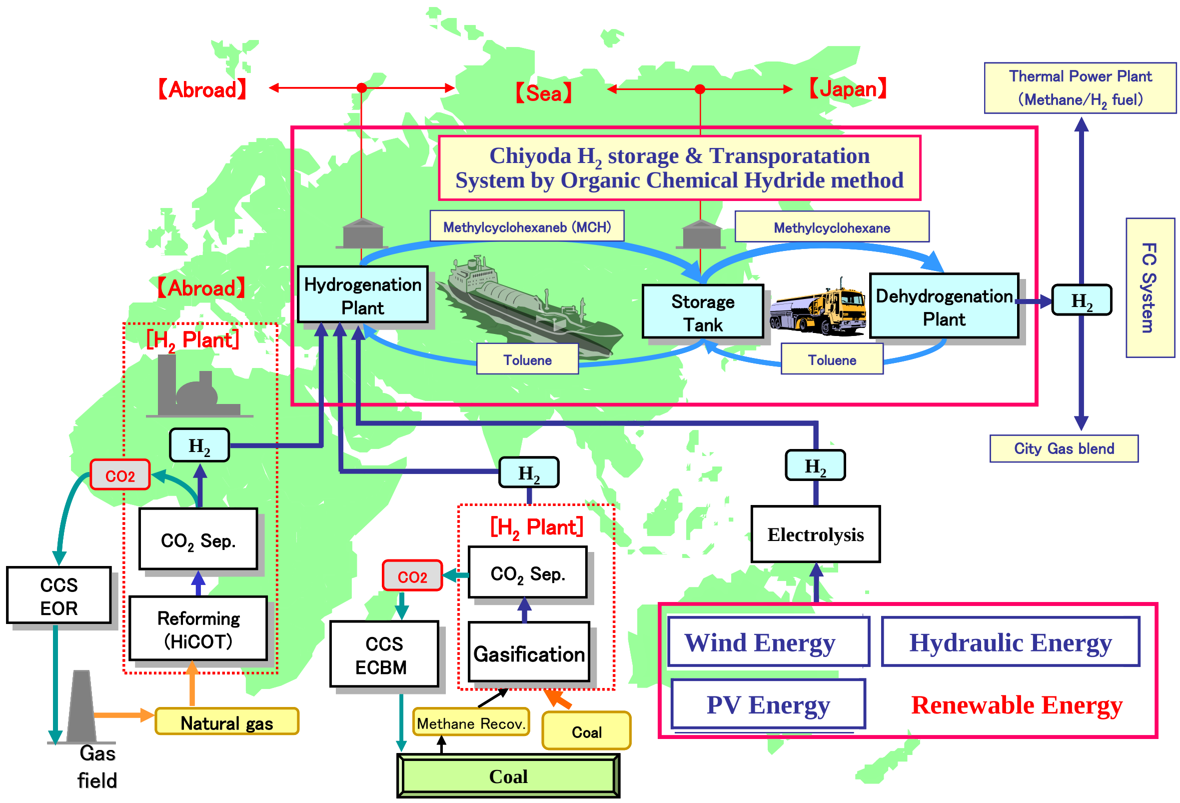

Fig.1 Hydrogen supply chain concept

3. Organic Chemical Hydride Method

Organic Chemical Hydride (OCH) method is a way to store and transport hydrogen under ambient temperature and pressure by using Liquid Organic Hydrogen Carrier (LOHC). Hydrogen is fixed to aromatic compounds such as toluene by hydrogenation reaction, and toluene is converted to mehylcycloheane (MCH). Toluene and MCH are both of gasoline components, and those are in the liquid state under ambient condition. Hydrogen is generated by dehydrogenation reaction from MCH at the hydrogen using site. Toluene is recovered and recycled back to hydrogenation site and reused as hydrogen carrier.

Table 1 shows the comparison of physical properties of typical organic hydride systems. Chiyoda employed toluene and MCH system, because that system has wide temperature range under which system can be kept the liquid state. Other system needs the solvent to keep the liquid state. Because toluene and MCH system are in the liquid state under from -95 to 101 ℃, solvent is not needed in any circumstance on the earth.

Table 1 Physical properties of typical organic hydride system

		MCH – Toluene		Cyclohexane – Benzene		Decalin – Naphthalene	
		Methylcyclohexane	Toluene	Cyclohexane	Benzene	Decalin	Naphthalene
Fomura		C_7H_{14}	C_7H_8	C_6H_{12}	C_6H_6	$C_{10}H_{18}$	$C_{10}H_8$
M.W.		98.19	92.14	84.16	78.11	138.25	128.17
State at room temp.		Liquid	Liquid	Liquid	Liquid	Liquid	Solid
Density (g/cm^3)		0.7694	0.8669	0.7791	0.8737	0.8963	0.9752
mp. (℃)		−126.6	−95.0	6.5	5.5	cis : −43.0 trans : −30.4	80.3
bp. (℃)		100.9	110.6	81.0	80.1	cis : 194.6 trans : 185.5	218.0
Hydrogen Storage Density	(wt%)	6.2		7.2		7.3	
	(kg-H_2/m^3)	47.4		56.0		65.4	

Fig.2 shows the hydrogen storage density. MCH has 6.1wt% of gravimetric hydrogen content and 47% of volumetric content theoretically. Other plots show the practical values including container in a small-scale storage for FCV. It is considered that theoretical value is not so much changed in the case of OCH method, since storage condition is ambient and special container is not needed.

In the OCH method, hydrogen gas volume is reduced to <1/500 under ambient condition. Natural gas volume is reduced to <1/600 by liquefaction using -163 ℃ as LNG. Although in the liquefied hydrogen (LH_2) method hydrogen gas volume is reduced to <1/800, the method needs -253℃ and boil off gas treatment. OCH method is suitable in a large-scale storage and transportation, since the method has relatively high storage density in spite of ambient condition and no loss of hydrogen during long term massive storage.

In Japan, OCH and LH_2 method are under development as a large-scale hydrogen storage and transportation method. The practical use target of LH_2 method by large LH_2 tanker is 2025. The both of toluene and MCH have been transported commercially by middle range class chemical tanker which more than 50,000 tons of toluene or MCH is transported by one ship. The amount of hydrogen transported by above chemical tanker is more than 3,000 tons of hydrogen which amount equals to fuel to 600,000 FCVs with 5kg hydrogen.

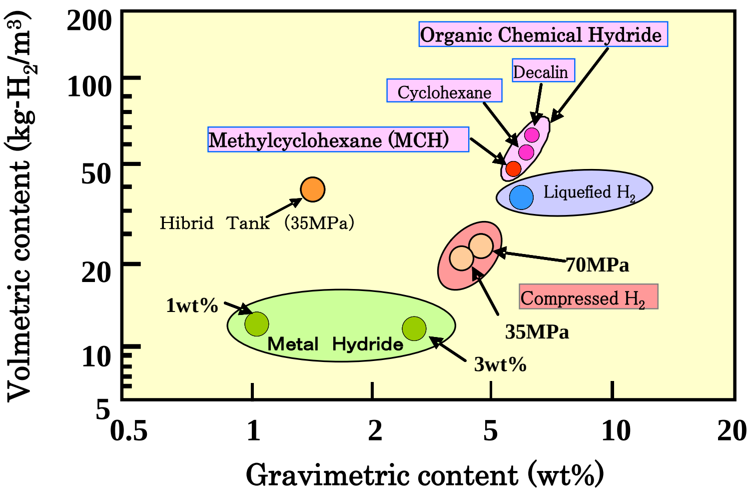

Fig.2 Gravimetric and volumetric content of hydrogen

OCH method was investigated in the Euro-Quebec project in 1980's as MCH method to transport hydrogen from the hydraulic power in Canada to Europe. However, since the dehydrogenation process did not exist in those days, the method has not been established until at present.

Fig.3 shows the scheme of OCH method. The hydrogenation process from toluene to MCH has been well commercialized process from 1970's. Since the yield of MCH is more than 99%, the hydrogenation process is well established.

The conventional chemical storage tanks can be utilized as toluene and MCH storage, and marine transportation is well commercialized mentioned above. The land carriage is also well commercialized by chemical tracks on the road and the freighter on the railways. Therefore OCH method will be established by the development of novel dehydrogenation process.

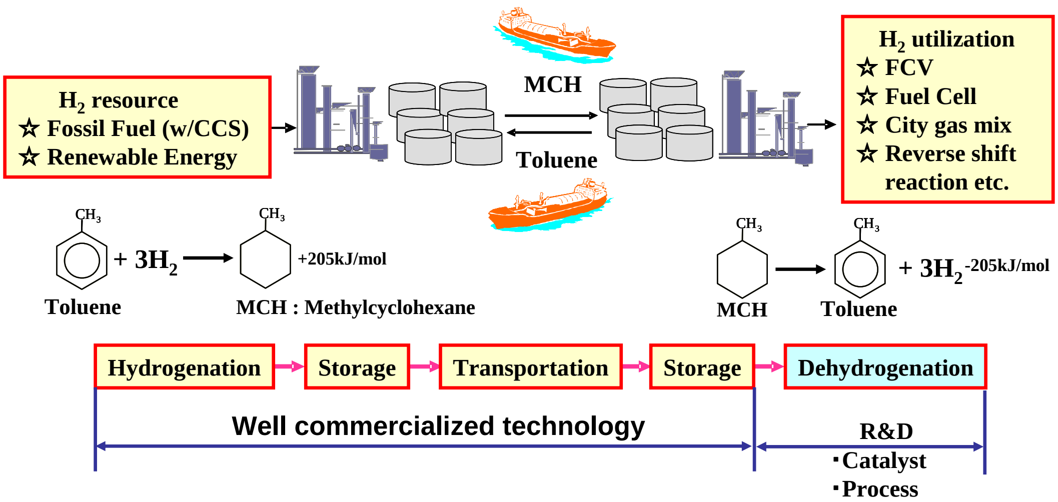

Fig.3 Scheme of OCH method

4. Dehydrogenation Catalyst

Chiyoda Corporation has been developed the high performance and long life dehydrogenation catalyst for the commercialization, Fig.4 shows the estimated catalyst surface model. Platinum cluster (<1nm) is impregnated to alumina carrier of which pore size is well controlled uniformly to increase the catalytic activity, and the platinum cluster is partially modified with sulfur atoms to prevent the coking. Although usual platinum impregnated alumina carrier is egg shell type in which the platinum cluster is disperse in the only rim of the catalyst pellet, developed catalyst is in the uniform type in which the platinum cluster is well disperse around inside of catalyst pellet uniformly.

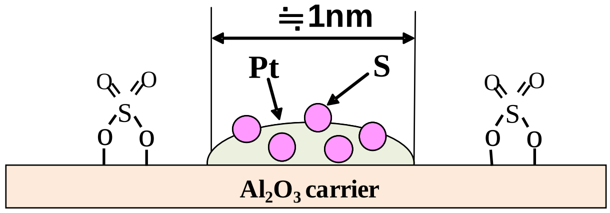

Fig.4 Estimated surface model of developed dehydrogenation catalyst

Fig.5 shows the result of the catalyst performance test. The developed dehydrogenation catalyst has an excellent performance, MCH conversion > 95%, toluene selectivity >99.9% and hydrogen yield is more than 95% under the condition of around 350℃, 0.3MPa and LHSV $=2.0h^{-1}$. The hydrogen can be generated more than 1,000Nm^3-H_2/h/m^3-cat. Catalytic performance is well stable more than 1year continuously. The catalyst will be exchanged after deactivation of the catalyst, platinum is recovered from the spent catalyst. Since the recovered platinum will be used for the catalyst production for next charge, catalyst cost is reasonable as same as petrochemical catalysts. Chiyoda Corporation has also developed the dehydrogenation process using developed catalyst. The catalyst can be used in the simple fixed bed tubular reactor. The development status is in the demonstration step.

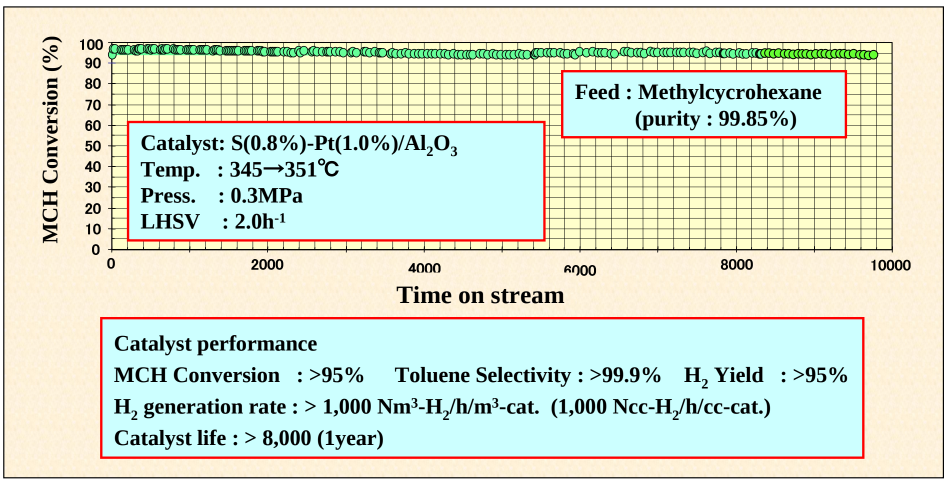

Fig.5 Result of catalyst performance test

5. Demonstration

Chiyoda Corporation has a plan to demonstrate the whole system of the OCH method, which include hydrogenation/dehydrogenation process and toluene recycle system in a scale of 50Nm^3/h in 2013 in Yokohama, Japan. Fig. 6 shows the image of the demonstration plant. The both of the hydrogenation and dehydrogenation reactors have the practical catalytic tube to be used in the commercial plant.

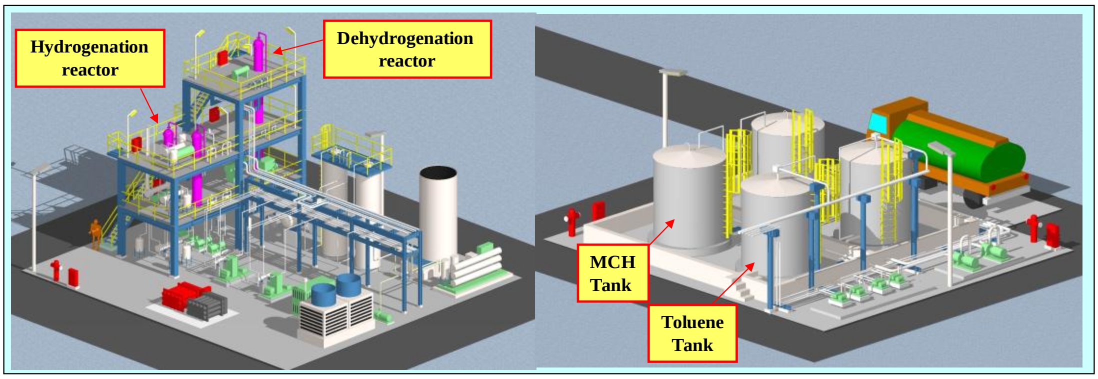

Fig. 6 Image of the demonstration plant for OCH method

6. Conclusion

OCH method is suitable for a large-scale storage and transportation of the hydrogen energy. Chiyoda Corporation has been developed a novel catalyst for the dehydrogenation reaction and dehydrogenation process. The development status has been shift to the demonstration step. Chiyoda Corporation has a plan to demonstrate the OCH method with demonstration plant (50Nm^3/h) in Yokohama, Japan in 2013. After demonstration, the development will have completed and the system will be in the commercial step.

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