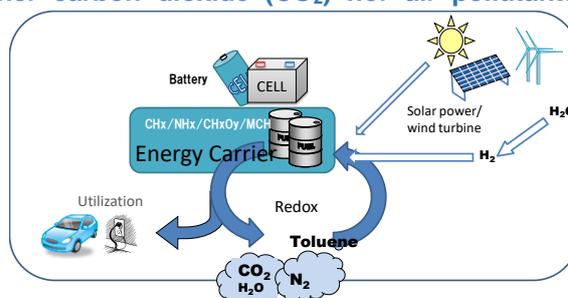


Accounts of Materials & Surface Research

Production, storage, utilization of hydrogen

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Hydrogen has been utilized in many production and purification processes of chemical compounds so far, including ammonia synthesis, petroleum refinery, synthesis gas conversion (e.g. methanol synthesis, Fischer-Tropsch synthesis), reduction of mineral resources. Recently, hydrogen is expected as a clean secondary energy source in the future. Hydrogen is producible from various resources including conventional and unconventional resources. Additionally, combustion process of hydrogen exhausts neither carbon dioxide (CO₂) nor air pollutants excepting NO_x from the air in the case of hydrogen internal combustion. Since transportation systems of gaseous hydrogen has not been established yet, use of hydrogen as an energy resource is limited in status quo despite such advantages. Many transportation systems for hydrogen have been proposed and investigated. In this review, recent trend on the production, storage, and utilization of hydrogen are summarized.



Keyword: Hydrogen; Production; Storage; Utilization; Catalyst

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Kent Takise has researched on catalysis for production and transportation of hydrogen, by which he received Ph. D. degree at Waseda University in 2019. Research focus was steam reforming of aromatics and dehydrogenation of methylcyclohexane using catalytic surface protonics. Continuous supports were given from Japan Society for the Promotion of Science as a national research fellow.



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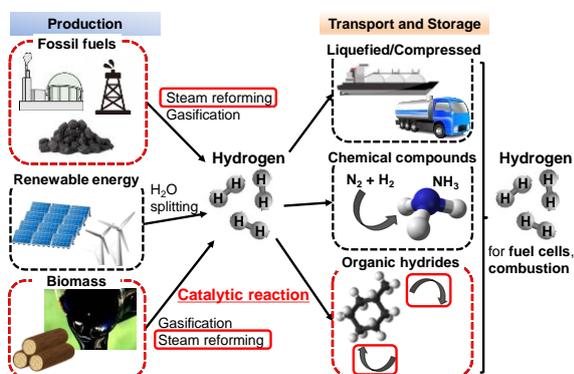
Production, storage, utilization of hydrogen

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Waseda Univ.

1. Introduction

Considering the sustainability, production, storage/transport, and utilization of hydrogen are very important. Now, gaseous hydrogen is produced to satisfy industrial-level demand for hydrogen. The world production ratios of hydrogen show 48% production from methane steam reforming, 30% from by-production from fossil oil (including naphtha steam reforming), 18% from gasification of coal, and 4% from water electrolysis^{1,2}. Hydrogen production still relies mainly on fossil fuels under the status quo. Hydrogen has raised great expectations as a clean secondary energy for use in a carbon-free hydrogen society in future. Also, hydrogen has been applied in many production and purification processes of chemical compounds. Representative processes demanding hydrogen include ammonia synthesis, petroleum refinery, synthesis gas conversion (e.g. methanol synthesis, Fischer–Tropsch synthesis), and reduction of mineral resources. Recently, hydrogen utilization on fuel cells are increasing in home, vehicle and so on. In this review, we summarize situations and recent trends on Figure



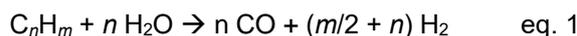
1 Flow of hydrogen production, storage/transport and utilization.

hydrogen production, transport/storage, and utilization.

2. Hydrogen Production

2.1 Catalytic steam reforming

Catalytic steam reforming is the most generally used method for mass production of hydrogen for ammonia synthesis and other uses. Hydrogen or synthesis gas is synthesized from hydrocarbons and steam, as shown in the following equations.



Although the steam reforming reaction (eq. 1) is an endothermic reaction, the water gas shift reaction (eq. 2) is an exothermic reaction. Both reactions proceed simultaneously, but steam reforming requires large amounts of thermal energy³. Accordingly, the reaction is conducted at high temperatures of around 973–1173 K using multiple heat-exchangers. Lowering of the reaction temperature is desired for higher-efficiency hydrogen production. Generally, natural gas (methane) or naphtha has been used as a raw material for reasons of cost^{4,5}. For that reason, methane and naphtha have tended to be the main research objects of steam reforming. That attention notwithstanding, steam reforming of other fuels (e.g., methanol⁶⁻⁸, ethanol⁹⁻²⁰, dimethyl ether^{21,22}, aromatics²³⁻³⁵, and glycerol³⁶⁻³⁸) has been investigated extensively to allow for raw-material diversity.

As an active metal for industrial steam reforming processes, Ni metal is commonly used because of its high activity and low cost³. Steam reforming

over Ni^{36,39} and other metals such as Co^{9-11,32}, Fe^{33,35,40}, Pt¹², Pd^{6,8,21}, Rh^{34,41}, Ru³⁸, and Ir³⁷ were also investigated in the study phase. The role of an active metal during steam reforming is generally dissociation of C–H bonding and C–C bonding of raw-material hydrocarbons. These active metals were supported over metal oxides to maintain high metallic dispersion. The main required functions for an oxide support during steam reforming are sintering inhibition of active metals and affinity or adsorption ability for steam and hydroxyl group to support the reaction. Both functions are also important for coke suppression, which is the main cause of catalytic deactivation during steam reforming⁴². Deposited coke covers surficial active sites and causes catalytic deactivation during steam reforming^{42,43}. Actually, coke is formed through step-by-step condensation of adsorbed hydrocarbons; several types of deposited coke have been reported^{44,45}. First, adsorbed hydrocarbons i.e. C_nH_m(ad) are dehydrogenated to surficial carbide (C α)^{44,45}. This C α is converted to C γ (whisker carbon), C β (polymeric or amorphous films of carbon) or graphite carbon with further condensation^{44,45}. The C α and C β are more reactive or more removable than the others⁴³⁻⁴⁵. Graphite carbon and whisker carbon tend to form at higher temperatures⁴³⁻⁴⁵.

2.2 Suppression of coke deposition

Accelerating oxidative gasification of surficial hydrocarbons or reactive coke species is beneficial to avoid hydrocarbon condensation and coke formation⁴³. Gasification of those species to CO or CO₂ can be accelerated using dissociated water or mobile lattice oxygen. Moreover, the addition of alkali-earth metal can promote water activation on a catalytic surface^{46,47}. Substitution of lattice metal ions can increase lattice oxygen

mobility^{23,25,48,49}. Highly dispersed active metals can control the coke formation rate because coke deposition occurs more on aggregated metals⁵⁰. Additionally, highly dispersed coke offers a larger interface between active metals and metal oxides at which hydrocarbons can react with activated water or mobile lattice oxygen. Coke suppression methods have gathered much attention for maintaining catalytic stability during steam reforming.

2.3 Low temperature steam reforming

Catalytic steam reforming, an endothermic reaction, is generally conducted at high temperatures of 973–1173 K, so a catalytic reaction occurring at such high temperatures entails some important issues related to the necessity for multiple heat exchangers and the aggregation of active metals. At lower temperatures, steam reforming of several raw materials (e.g., methane⁵¹⁻⁵⁵, ethanol^{52,56}, dimethyl ether: DME⁵⁷) has been accomplished in an electric field. Platinum-supported or palladium-supported CeO₂ or Ce_xZr_{1-x}O₂ catalysts were used during such low temperature steam reforming in the electric field. Sekine *et al.* reported that methane steam reforming proceeded at 423 K with 3 mA of electric field application⁵¹⁻⁵⁵. Manabe *et al.* clarified that a surficial proton hopping phenomenon activated methane dissociation over Pd/CeO₂ catalyst^{54,58}. In addition, Okada *et al.* reported that reaction rates of methane steam reforming in the electric field were higher when deuterium-containing isotopes i.e. CD₄ and D₂O were introduced compared to methane (CH₄) and steam (H₂O)⁵⁵. Accordingly, an “inverse” kinetic isotope effect (KIE) was confirmed during steam reforming in the electric field, which suggested that the reaction was promoted in the electric field by accelerated protons⁵⁵. The electric field

promoted the catalytic reaction with surficial ionic species at especially low temperatures.

In addition, tri-reforming and dry reforming of methane have been conducted in an electric field over Ni supported 10 mol%La-ZrO₂-based catalyst⁵⁹⁻⁶¹. In the case of tri-reforming, a lower reaction temperature and Mg addition suppressed methane combustion⁵⁹. Yabe *et al.* described that methane was activated with surficial protonics through the reactions, even in water-lean conditions⁵⁹⁻⁶¹. Results show that the catalysts exhibited dry reforming or tri-reforming activity below 473 K⁵⁹⁻⁶¹. Lower temperatures suppressed coke by-production from methane, which was crucially important for catalytic stability during the reaction⁶⁰.

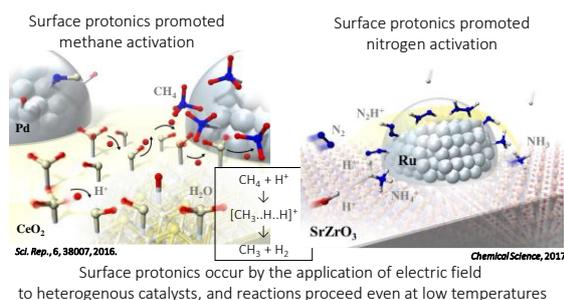


Figure 2 Schematic image of catalytic reaction in the electric field.

2.4 Steam reforming of heavy hydrocarbons

In the case of steam reforming of aromatics, reactant aromatics tend to be converted to coke as a byproduct on the catalytic surface. Generally, a catalyst consists of an oxide support and active metals. Consequently, second metal addition e.g. alkali-earth metals and lanthanum can promote water dissociation, which is important for gasification of coke precursors on the surface^{46,47,62}. Additionally, the redox property of the support is important because mobile lattice oxygen in/on supports can facilitate oxidation of hydrocarbons and coke precursors^{23,48,49}. The lattice oxygen mobility or conductivity requires

lattice oxygen vacancies. Consequently, the lanthanum (La³⁺) site of LaAlO₃ support was partially substituted with strontium (Sr²⁺) to form vacancies because of electron compensation. Active metal supported La_{0.7}Sr_{0.3}AlO_{3-δ} catalysts were used for toluene steam reforming. Moreover, the electric field can promote lattice oxygen mobility.

Although coal is known as an abundant and omnipresent fossil fuel⁶³, it has low hydrogen capacity of 4–6 wt%. For that reason, the amount of H₂ produced against CO₂ is correspondingly low^{63,64}. By adopting coal gasification, a high probability of producing high-purity hydrogen exists and NO_x and SO_x formation is suppressed, so it is easier to segregate CO₂⁶⁴⁻⁶⁶. Gasification proceeds at 1273–1723 K using crushed dry or slurry coal and an oxidant, which is usually air, oxygen or steam⁶³. Water gas shift reactions are conducted after gasification to increase the hydrogen amount^{63,64}. Two reactors are used for water gas shift reactions: low-temperature reactors and high-temperature reactors^{63,67-73}. For high-temperature reactions at 598–723 K, Fe₂O₃-Cr₂O₃ catalyst is used^{63,67}. This catalyst has high resistance to sulfur or chlorine. However, an equilibrium limitation exists because the reaction occurs in a high conversion region⁶³. For low-temperature reactions at 473–523 K, Cu/ZnO/Al₂O₃ catalyst is used. This catalyst can be polluted by sulfur and chlorine because the adsorption of these impurities can occur easily in a low-temperature region⁶³. Some catalysts such as Co-Mo/Al₂O₃ are useful in a wider temperature region without being adversely affected by impurities⁶³. Although coal gasification technologies were developed many years ago, some issues related to this process remain to be resolved. Most issues are related to the resistance of the apparatus around the gasifier⁶⁴. A feed

injector is said to last around 2–6 months. However, a lifetime of about a year is required for efficient operations. The life length is affected by sulfidation, corrosion, and the amount of fed steam⁶⁴. Moreover, thermocouples are used to measure the gasifier temperature, but these last for around 30–45 days⁶⁴. Much of the apparatus resistance must be greater to achieve high efficiency and low costs to compete with other resource-based methods.

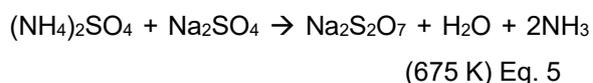
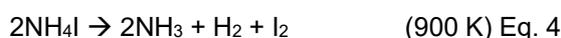
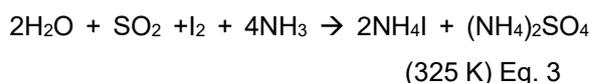
2.5 Photocatalysis, electrocatalysis, and thermal water splitting for hydrogen production

For networking a carbon-neutral society, hydrogen is anticipated for use as a clean secondary energy resource. As described so far, hydrogen production still relies today on fossil fuels and steam reforming, but hydrogen synthesis from omnipresent water or biomass can be substantial. Biomass is another resource for gasification. Tar and char are produced during gasification of biomass, even at high temperatures above 1173 K⁷⁴. Many gasifiers have been designed to lower reaction temperatures to achieve higher energy efficiency. Nevertheless, when a reaction is conducted at a low temperature below 1123 K, tar and char are more readily produced. To resolve this difficulty, Ni-based catalysts are used with steam reforming to convert these products to H₂, CO, and CO₂⁷⁴. Issues related to the deactivation of Ni catalysts in the reactor remain. Improvement of catalysts might engender breakthroughs providing higher efficiency during coal or biomass conversion to hydrogen.

Several means exist to produce hydrogen from water: photocatalysis, thermochemical cycle, and electrolysis. Photocatalytic water splitting has attracted attention because of the promise of producing clean hydrogen from water using solar power alone. In the 1970s, Fujishima and Honda

reported the photocatalytic possibility of semiconductor TiO₂⁷⁵. Oxide semiconductors with a narrow band gap (below 3.0 eV) absorb visible light, by which electrons in a valence band are excited to the conduction band⁷⁶. Because the valence band is expected to be more positive than oxidation potential of water to O₂ (+1.23 V vs. normal hydrogen electrode (NHE)), the conduction band should be more negative than hydrogen production from protons. Consequently, the positive position of O 2p (at ca. +3.0 eV vs. NHE) makes it difficult to design a photocatalyst that can proceed both reactions above. Furthermore, the recombination of excited electrons and holes is problematic. It is well-known that the *d*-orbital causes recombination. Consequently, *d*0 or *d*10 electron configuration is necessary for efficient photocatalysis⁷⁶. Although many contributions have been given (e.g. Z-scheme) for this attractive reaction, the reaction rate to produce hydrogen is not quite sufficient for mass production presently.

Thermochemical water splitting is a combination of chemical reactions used to convert water to hydrogen and oxygen using heat. Exhaust heat from nuclear power or concentrated solar power (CSP) has been proposed as a heat source⁷⁷. Many cycles have been investigated for this reaction⁷⁷ (e.g., sulfur-iodine cycle⁷⁸, copper-chlorine^{79,80} and Zn/ZnO redox cycle⁸¹). Thermochemical reactions for sulfur-iodine cycle (an intensively investigated cycle in laboratory and large scale) were described as presented below, referred from the literature⁷⁹.





According to eqs. 3-7, all involved materials i.e. SO_2 , I_2 , NH_3 , and Na_2SO_4 , are regenerated in the process. The cycle consists of multiple reactions requiring high temperatures⁷⁹. Reportedly, the copper-chlorine-based cycle proceeded in lower temperature. However, the reaction network remained complicated^{79,80}. In addition, corrosive hydrochloric acid was produced as a byproduct by the copper–chlorine process. Recently, Davis explained a manganese-based cycle that proceeded at temperatures below 1273 K without toxic intermediates⁸². Required high temperatures and harmful or corrosive byproducts are common difficulties associated with these processes⁷⁷.

The most mature process for water splitting is alkaline water electrolysis, which produces 4% of the world's hydrogen production^{1,2}. For wider use of water electrolysis, some challenges remain: they include improvement of reliability and durability and reduction of energy consumption⁸³. Energy consumption through water electrolysis corresponds to the necessary cell voltage. Here, the cell voltage includes reversible potential for the electrochemical reaction and overvoltage⁸⁴. Decreasing the reaction barriers can lead to lower overvoltage during water electrolysis. Mainly three barriers currently impede electrolysis of water as a practical process: they are impediments to electrical application, transportation, and electrochemical reaction⁸³. First, conductivity improvement can lower the electrical barrier i.e. ohmic voltage. Potassium and sodium hydroxides are usually used in commercial electrolyzers to improve water conductivity^{83,84}. Second, physical transportation is inhibited by gas bubbles formed on the electrode and in the electrolyte solution⁸³. Finally, the reaction resistance is determined by activation energy of the hydrogen and oxygen formation reactions. Accordingly, development of

a stable and active electrode is important. Many studies have examined stable and active electrodes, better electrolyte conductivity (conditions and additives) and bubble treatment⁸³. In this section, we summarized recent trends on hydrogen production by various methods. Considering effective usage of renewable energy, further improvement in energy efficiency and better catalysts are anticipated.

3. Transportation and Storage of Hydrogen

3.1 Importance of hydrogen transport/storage

The possibility of using hydrogen as an energy depends on establishing its safe and cost-effective transportation and storage systems for gaseous hydrogen. Many concepts and technologies have been suggested.

Hydrogen has high specific energy with ability for production from various primary resources as a salient benefit^{85–87}. Even when compared with hydrocarbons, hydrogen has high energy density by weight. However, by volume, its energy density is low⁸⁵. To improve its low density to volume, better storage and transportation technologies must be developed. Two ways to store hydrogen physically can be used: hydrogen compression and liquefaction.

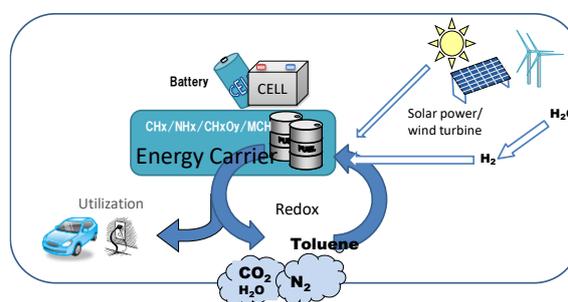


Figure 3 Various chemical methods for hydrogen storage.

3.2 Physical storage

Hydrogen compression is the most commonly

used method⁸⁵. The storage density of compressed hydrogen depends mainly on the storage pressure, although high-pressure storage tends to entail high costs because of high capital and storage requirements⁸⁷. Nowadays, the pressure used for hydrogen for storage is about 70 MPa⁸⁵. Because of its low storage density, storage quantities are small; only short-term storage is typically used⁸⁷.

Hydrogen can be stored as a liquid at temperatures below 20 K to increase the storage density by volume⁸⁵. By liquefying hydrogen, 70 g/L can be stored in tanks, reaching higher density of compressed hydrogen^{85, 86}. However, the capital costs to liquefy hydrogen are high and up to 30–33% of the hydrogen energy must be consumed simply for the compression process⁸⁵. Therefore, this method is suitable only for storage of large amounts. Other shortcomings associated with this method are that expensive materials must be used for storage tanks and to prevent vaporization loss of hydrogen. From the storage tank, 0.1–1% of hydrogen is vaporized each day⁸⁵. However, considering the associated costs, liquefied hydrogen is more efficient than pressurized hydrogen for long-term storage⁸⁷.

Material-based methods for hydrogen storage have attracted great attention. Several systems have been proposed for this purpose: hydrogen adsorbing alloys, metal-organic frameworks (MOF), and chemical hydrides including cyclic hydrocarbons as liquid chemical hydrides.

Metal-organic frameworks (MOFs) have attracted attention as a method to store hydrogen because of their reversibility and cyclability⁸⁸. An MOF is a porous material with high internal specific surface area^{88–90}. Actually, H₂ can adsorb on MOF by weak van der Waals force (1–10 kJ mol⁻¹ adsorption energy)⁸⁸. However, cryogenic temperatures or high pressure is required to

uptake H₂ sufficiently. The United States Department of Energy (DOE) has set an ultimate hydrogen storage goal of 7.5 wt%⁹¹. Although such materials have never been synthesized, computer-based simulation has identified ideal materials and structures to achieve short-term targets^{90, 92}. Han *et al.* reported that Li-doped MOFs (Li-MOF-C30: Li doped octahedral Zn₄O(CO₂)₆ cluster with aromatic carbon rings) achieved the 2010 DOE target i.e. gravimetric H₂ density of 6.0 wt% at 243–353 K and below 10 MPa⁹². Getman *et al.* reported that Li-based alkoxide has binding energy for H₂ that is too low to adsorb a sufficient amount⁹³. For a metal alkoxide system, Mg-based alkoxide was identified as a more promising functional group than other metal alkoxides⁹³. Many computing-based studies have been conducted for MOFs because computer calculations advantageous for optimizing several factors simultaneously i.e. theoretical H₂ uptake with any materials, structures, pressures, and temperatures. Through those theoretical calculations, ideal material combinations and structures can be designed at the molecular level^{88, 90}. Although many theoretical outputs have been reached to date, few materials have been synthesized practically or experimentally⁹⁰. A challenge of this research field is bridging the gap separating theoretical calculations and the practical synthesis of materials.

3.3 Chemical hydride

Various chemical hydrides can store hydrogen at high capacity. Chemicals that are often researched are ammonia, formic acid, methanol, dimethyl ether (DME) and methylcyclohexane. Ammonia is anticipated for use as a chemical hydride because of its high hydrogen capacity (17.6 wt%) and carbon-free structure^{94, 95}.

Production, transportation, and storage technologies and infrastructure already exist around the world industrially because 160 million tons of ammonia are produced every year⁹⁴. Ammonia decomposition catalyst is well studied for hydrogen extraction. The most practically used catalyst is Ni/Al₂O₃ because of its mechanical strength and heat resistance, and Cs-Ru/C catalyst is also well known^{94–96}. Ammonia can be transported in various ways i.e. ship, pipeline, and truck. Furthermore, several means exist to store ammonia. One is to store it in bulk with tanks over 50,000 t at 240 K and 0.1–0.8 MPa^{94, 95}. Another is to store it in smaller stainless-steel tanks of 1500 t under pressure⁹⁴. Unlike hydrogen, no evaporation loss occurs⁹⁵. Regarding safety, ammonia has no flammability in air, although the flammability of hydrogen and gasoline are very high⁹⁴. Unfortunately, liquid ammonia has high apparent toxicity, as reflected by its vapor pressure and its status as immediately dangerous to life or health⁹⁴. To reduce ammonia toxicity, various researchers are investigating metal amines, ammonium carbonates, and urea to store ammonia inside^{94,95}. Although ammonia-related compounds can resolve many transportation and storage related difficulties, it can be said that room remains for consideration and improvement of safe transportation and storage.

Formic acid, methanol, and DME are chemical hydrides that can be generated from CO₂ or CO with hydrogen. DME is synthesized from methanol dehydration⁹⁷. Formic acid, which is non-toxic, has hydrogen capacity (available H₂ divided by the stored material) of 4.4wt%⁹⁸. For the energy cycle of formic acid and CO₂, catalysts must be investigated both for dehydrogenation of formic acid and for hydrogenation of CO₂. The dehydrogenation of formic acid must be selective

and must suppress the reaction to produce CO and H₂O because CO is highly toxic and can poison Pt catalyst in the fuel cells⁹⁸. Catalysts with high selectivity during dehydrogenation have been investigated in both homogeneous and heterogeneous catalysts. Reportedly, Au, Rh, and Pd nanoparticles are active catalysts for the dehydrogenation of formic acid; also, bimetallics of Au or Ag to Pd have higher activity⁹⁸. However, development of CO₂ hydrogenation catalyst is still difficult. No heterogeneous catalyst to proceed CO₂ hydrogenation in the gas phase has been developed as a homogeneous catalyst. This result derives from the difference of activation energy of CO₂ hydrogenation in gas phase and aqueous solution (gas phase: $\Delta G = +33 \text{ kJ mol}^{-1}$, aqueous phase: $\Delta G = -4 \text{ kJ mol}^{-1}$)⁹⁸. Few catalysts reportedly complete the reversible cycle of formic acid and CO₂. One reported catalyst is Ir complex homogeneous catalyst in aqueous solution^{98, 99}. Another is Pd-Ag nanoparticle supported on amine-functionalized silica or phenylamine-functionalized mesoporous carbon^{98, 100}.

Chemical hydride method consists of reversible hydrogenation and dehydrogenation reactions occurring between aromatic and naphthene compounds (cycloalkane). At hydrogen supplying sites, aromatics are hydrogenated to naphthene compounds to store hydrogen in its structure. The opposite reaction, i.e. dehydrogenation of naphthene, is conducted to extract hydrogen at consuming sites. This process requires no large capital investment because conventional transportation or storage infrastructure for fossil fuels is useful¹⁰¹. Many compounds have been proposed for this system. Recently, a perhydro dibenzyltoluene/debenzyltoluene cycle was investigated because these compounds have neither toxicity nor explosivity. Additionally, they are liquid at a wide range of temperatures (243–

633 K)¹⁰². The most well-known cycles are the cyclohexane/benzene cycle, methylcyclohexane (MCH)/toluene cycle, and decalin/naphthalene cycle. The respective gravimetric H₂ capacities of those cycles are 7.1%, 6.1%, and 7.2%¹⁰¹. Despite low H₂ capacity, the MCH/toluene cycle has been the most investigated because of its nontoxicity and easy-handling nature i.e. a wider range of liquid phase 178–374 K^{101, 102}.

Feasibility of the MCH–toluene cycle depends on the stability and efficiency of catalytic dehydrogenation processes¹⁰¹. This reaction has been commonly performed on Pt-supported alumina catalyst because of its high catalytic activity and selectivity^{101, 103–106}. However, Pt-supported catalyst is readily deactivated by coke formation^{101, 103}. Coke precursor might be MCH, toluene, or intermediates (e.g., methylcyclohexadiene): it remains controversial¹⁰¹. For example, Chai *et al.* described coke precursor formed by methylcyclohexadiene differently adsorbed from the case of main dehydrogenation reaction¹⁰⁷. Pacheco *et al.* reported that coke was produced by the reaction between gaseous toluene and a surface carbon skeleton caused by dissociative adsorption of MCH^{108, 109}. Many attempts have been conducted for prevention of coke, such as highly dispersed platinum metal¹¹⁰, second metal addition^{107, 111}, and pre-sulfidation of active metal¹⁰⁷.

Because catalytic dehydrogenation is an endothermic and reversible reaction, a strong limitation is imposed by thermodynamic equilibrium. Consequently, dehydrogenation was usually performed at temperatures higher than 623 K¹⁰¹. For better efficiency of chemical hydride cycles, either or both waste heat utilization and lower reaction temperature are necessary for the dehydrogenation process. Regarding power generation from hydrogen, exhaust heat from fuel

cells (re-electrification) might as well be used for dehydrogenation¹⁰¹. Fuel cells of several types exist, but low-temperature fuel cells (i.e. polymer electrolyte fuel cells and phosphoric acid fuel cells) are not applicable in such a temperature region. Accordingly, only high-temperature fuel cells (i.e. molten carbonate fuel cells and solid oxide fuel cells) are combined with chemical hydride systems for central power generation under the status quo. The lower reaction temperature can reduce energy consumption and can enable recovery of lower-grade heat during dehydrogenation^{101, 112–114}. Two general schemes exist to achieve low-temperature dehydrogenation. First is the introduction of heteroatom(s) such as nitrogen (N) into cyclic organic ring(s). Dehydrogenation of hetero-rings requires lower enthalpy gain than with “pure” cycloalkane¹⁰². However, N-containing cycloalkanes have some important shortcomings: lower H₂ gravimetric densities and melting points at high temperatures¹⁰². The other scheme is exceeding equilibrium limitations at low temperatures. Low temperature dehydrogenation has been attempted to exceed severe equilibrium limitations using catalytic membrane reactors^{115–119}, liquid-film type catalysts^{120–123}, and wet-dry-multiple phase conditions^{124, 125}. General concepts related to them have been separating products i.e. hydrogen and aromatics from the reaction field. Although those concepts are quite reasonable, no system has reached the demonstration phase. Therefore, some room for improvement exists for brand-new methods of low-temperature MCH dehydrogenation. MCH dehydrogenation was also conducted on Pt/CeO₂ catalyst in the electric field at low temperature (423 K). This reaction is generally performed on Pt-supported catalysts at temperatures higher than 623 K because of thermodynamic equilibrium limitation. Electric field

promoted proton conduction on CeO₂ support, and accelerated proton collided with methane activating C-H cleavage over Pd metal^{54, 55, 126}. Although this reaction has an equilibrium limitation in the low temperature region (5.5% at 423 K), Pt/CeO₂ catalyst showed 21.6% catalytic activity at 423 K in the 3 mA of electric field. Hydrogen partial pressure was positively correlated with the dehydrogenation rate despite reversibility of the reaction. In addition, *inverse* kinetic isotope effect (KIE) was confirmed in the electric field. Therefore, proton conduction over Pt/CeO₂ was regarded as promoting dehydrogenation of MCH. According to *operando* IR measurements, toluene desorption was facilitated in the electric field. Based on these results, we concluded that proton conduction rendered dehydrogenation “*irreversible*” with proton collision and toluene desorption¹²⁶. Further investigations for efficient hydrogen storage/transport are anticipated.

Table 1 Various hydrogen storage/transport methods.

	Hydrogen (gas)	Liq. Hydrogen	Ammonia	Methylcyclohexane
Molecular weight	2.0 g/mol		17.0 g/mol	98.2 g/mol
Combustion enthalpy	286 kJ/mol		382.6 kJ/mol	
Boiling point	-253°C	-253°C	-33.4°C	101°C
Weight hydrogen density	100 wt%	←	17.8 wt%	6.16 wt%
Volumetric hydrogen density	2 kg/100 L (35 MPa)	7.06 kg/100 L	12.1 kg/100 L (liquid)	4.73 kg/100 L
Reaction enthalpy for hydrogen production	-	0.899 kJ/mol-H ₂	30.8 kJ/mol-H ₂	59.4 kJ/mol-H ₂
Explosion limit	4.1~74.2vol%	←	15~28 vol%	1.4~6.7 vol% (toluene)
Toxicity		←	LCL0: 1500 ppm TCL0: 20 ppm	LDL0: 50 mg/kg TCL0: 200 ppm

4. Hydrogen utilization as a chemical feedstock

4.1 Hydrogen as a chemical source

Hydrogen gas is used for ammonia mass production using the Haber–Bosch process. Ammonia is widely used as a raw material for nitrogen fertilizers, chemical dyestuffs, resins and pharmaceuticals. Also, as mentioned in previous section, ammonia has attracted attention as a

hydrogen carrier. Consequently, ammonia synthesis is an increasingly important chemical process. At the beginning of twentieth century, the Haber–Bosch process enabled industrial nitrogen fixation, in which atmospheric nitrogen (N₂) is converted to ammonia (NH₃) by reaction with hydrogen (H₂) over an iron-based catalyst. This process requires an approximately 673–773 K reaction temperature and 20 MPa of pressure^{127, 128}. The original catalyst found by F. Haber was developed by A. Mittasch. Magnetite (Fe₂O₃) was promoted by irreducible oxides, K₂O and Al₂O₃ at first, then also CaO^{127,129}. Ertl discovered that Al₂O₃ played a role as a structural promoter to stabilize α -Fe phase forming spinel Al₂FeO₄ internally¹³⁰. Additionally, CaO suppressed thermal sintering of Fe during the reaction. Also, K₂O facilitated Fe-based catalyst donating electron with its basic features¹³⁰. Such promoted Fe catalysts are still used today for ammonia production.

4.2 Ammonia synthesis

In the 1970s, Aika *et al.* reported that Ru-based catalysts showed much higher activity than iron-based catalysts in the presence of alkali and alkali-earth metal promoters such as Cs, K, and Ba^{131, 132}. Ammonia synthesis can be performed under milder conditions on Ru catalysts i.e. lower temperature and lower pressure, and Kellogg commercialized ammonia synthesis plants using graphite-supported Ru catalyst in 1992¹³³. Recently, additional investigations have been undertaken for Ru, Co and Fe catalysts for obtaining higher catalytic activity at lower temperatures and lower pressures^{134–141}. Manabe *et al.* reported that a 9.9 wt%Cs/5.0wt%Ru/SrZrO₃ catalyst achieved a 30 mmol g-cat⁻¹ h⁻¹ of maximum ammonia synthesis rate (i.e. very high rate) with electric field addition

¹³⁸. According to their results related to *in-situ* IR measurements (IR measurement in the electric field addition), formation of N_2H was confirmed in the electric field ^{138,139,141}. They concluded that the electric field induced proton hopping on the support $SrZrO_3$, and that it accelerated N_2 conversion to N_2H over supported Ru metal ^{138,139}. The apparent activation energy decreased from 121 kJ mol^{-1} to 37 kJ mol^{-1} because of the dissociation reactivity of N_2H rather than N_2 ^{138,139}. Proton conductivity was also confirmed on a $Co/Ce_{0.5}Zr_{0.5}O_2$ catalyst during ammonia synthesis in an electric field ¹⁴⁰. The rate limiting step of ammonia synthesis is well known to be dissociation of adsorbed N_2 molecules. Consequently, formation of the proton-derived species facilitated the rate limiting step of ammonia synthesis with electric field addition.

4.3 Hydrotreating

Hydrotreating is an important process conducted during petroleum refining. Actually, it involves desulfurization, denitrification, and heavy oil cracking, thereby supplying hydrogen gas. The content ratio of sulfur in crude oil is notably higher than other impurities such as nitrides, nickel, and vanadium. Sulfur-containing species contained in fuel are converted to SO_x after combustion in engines. Then they contribute considerably to air pollution and acid rain. Additionally, sulfur is regarded as a typical poison for catalysts. Therefore, sulfur contents are not only harmful themselves: they also inhibit catalytic removal of other harmful substances such as NO_x and hydrocarbons (HC). The greater the degree to which the regulation limit of sulfur content has been restricted, the more necessary development of desulfurization catalyst has become ¹⁴².

Sulfur contained in thiol, sulfide, disulfide, and thiophene is hydrogenated and removed as H_2S

through hydrodesulfurization processes. Alumina-supported MoS_2 -based catalysts are generally used and investigated for hydrodesulfurization ^{142–144}. Actually, both Co and Ni promotion to the MoS_2 structure have been well known as effective to achieve higher catalytic activity during reaction ^{142–146}. Many experimental investigations and DFT calculations have demonstrated that Co or Ni promotes substitution of Mo sites at the edge of MoS_2 layers and synthesized Co-Mo-S or Ni-Mo-S structures ^{143,144,146,147}. However, the exact structure of substituted sites has been debated extensively for a long time ^{147,148}. Recently, the most probable structure of the active site was observed experimentally on industrial-type multilayers ¹⁴⁹ and a single-crystal under working conditions ¹⁵⁰. Co was attached preferentially on the S-edge termination of each layer ^{147–150}. Reportedly, the addition of Co or Ni weakened Mo-S bonding on S-edge of MoS_2 , then formed vacancies at the edge promoted desulfurization ^{147,150}. Several revealed schemes and facts might lead to better catalytic design for oil purification under severer regulations for sulfur.

4.4 Fuel synthesis

Commonly, C_1 chemistry is defined as chemical processes converting methane or synthesis gas ($CO + H_2$) to more valuable chemical products or chemical feedstocks. Methane is a main component of natural gas, for which the “shale gas revolution” has discovered large resources and reserves. Direct conversion of methane has been investigated for decades to improve the efficiency and cost-effectiveness of chemical process ¹⁵¹. Despite outstanding researching efforts and achievements ^{152–159}, industrial applications remain limited because of their low yield or selectivity of products and stability of catalysts ¹⁵¹. For industrial production, methane is first

converted to synthesis gas with catalytic steam reforming. Synthesis gas is produced mainly by steam reforming of methane or naphtha and gasification of coal or biomass. Consequently, chemical conversion of synthesis gas has been examined extensively and developed world-wide. Fischer–Tropsch synthesis (FTS), a well-known catalytic reaction, produces functional liquid hydrocarbons from synthesis gas. This process, invented by F. Fischer and H. Tropsch in Germany of the 1920s, was intended to produce liquid fuels from coal resources for strategic reasons independent of economic aspects¹⁶⁰. Both Co-based and Fe-based catalysts were generally used for commercial processes at temperatures of 473–613 K and pressures of 1–6 MPa^{160,161}. Later, FTS processing using Fe-based catalyst was commercialized in Sasolburg, South Africa in 1955 under their circumstances of political sanctions, but with their large coal resources¹⁶¹. Actually, Fe-based catalysts were more likely to by-produce carbon accumulation¹⁶². In the 1990s, Sasol Company successfully introduced commercial fluid-bed FTS with a slurry Fe-based catalyst^{160,161}.

Actually, Co-based catalyst is more suitable to obtain longer chain hydrocarbons (C_1 to C_{100}) at lower temperatures (423–463 K)^{160,163}. There, metallic cobalt nanoparticles were supported on high-surface-area oxides such as SiO_2 , Al_2O_3 , and TiO_2 . In addition, recent industrial catalysts were promoted using precious metals such as Pt, Ru, and Re to control coke formation¹⁶³. Fixed bed reactors are appropriate for low-temperature FTS aimed at higher average molecular chains¹⁶⁰. Fe-based catalyst tends to synthesize olefinic hydrocarbons with lower average molecular weight¹⁶⁰. Alkali promoted iron carbide catalyst is generally used at higher temperatures below 613 K^{160,163}. As described above, different features

between two active metals (Co and Fe) were observed. Many investigations of product selectivity, catalyst lifetime, and other issues have been undertaken to overcome catalytic issues during FTS^{164–168}.

Methanol is regarded as an efficient form for transportation and storage of synthesis gas because it can exist in a liquid state at room temperature and pressure. The kinetics and mechanism of catalytic methanol synthesis over Cu catalyst have been discussed in many works^{169–171}. Actually, ZnO addition has been revealed as facilitating Cu-based catalyst during the reaction^{170–173}. Consequently, industrial synthesis of methanol from CO and H_2 is usually conducted over Cu/ZnO/ Al_2O_3 catalyst¹⁷⁴. Carbon monoxide (CO) adsorbs on Cu-active metal, and H_2 to ZnO^{170,171}. The adsorbed CO is then hydrogenated to oxygenate intermediates such as formate species. Subsequently, they are stabilized on a stepped Cu surface^{171,174}. Therefore, dispersion of Cu metal is quite important for this reaction¹⁷⁴. Additionally, it has been reported that ZnO doping is necessitated for the stabilization of oxygenate intermediates e.g. formate species and aldehyde species^{169,174}. Here, formate species are the most stable and longest-lived intermediates¹⁶⁹. Accordingly, synergetic effects of Cu and ZnO are substantial for the hydrogenation of formate species¹⁷¹.

A complex chemical reaction network is built for methanol synthesis. Similar intermediates are formed in both cases of hydrogenation of CO or CO_2 ¹⁷⁵. Therefore, methanol synthesis from CO_2 and H_2 has also been investigated on similar Cu-based catalysts. This reaction can be regarded as a CO_2 utilization method using hydrogen. Consequently, one can surmise that catalytic methanol synthesis will continue to gather much attention.

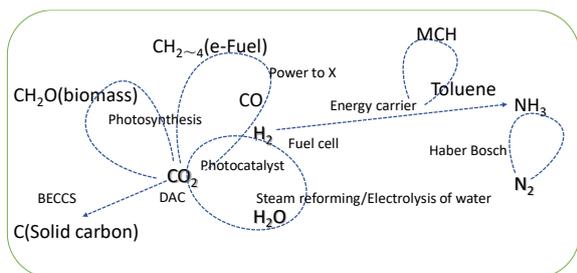


Figure 4 Hydrogen as a chemical feedstock.

5. Hydrogen as a secondary energy

5.1 Situation and trend on the hydrogen energy

Currently, hydrogen is regarded as a promising candidate for secondary energy because it is producible from various resources including conventional and unconventional resources. Additionally, the hydrogen combustion process produces neither carbon dioxide (CO₂) nor air pollutants except NO_x from the ambient air in the case of hydrogen internal combustion^{176,177}. This feature is highly beneficial considering that regulation of CO₂ and air pollutant emissions are expected to become more restricted in the future. Despite such benefits, the use of hydrogen as an energy resource is limited under the status quo because transportation systems using gaseous hydrogen have not been established yet. Many hydrogen-based transportation systems have been proposed and assessed during the last few decades, as described in previous section. Hydrogen-fueled internal combustion has been investigated for automobiles as an alternative to fossil fuels¹⁷⁷. As clean-emission vehicles, fuel cell powered vehicles (FCV) and battery-electric vehicles (BEV) are anticipated as candidates for future social applications. Hydrogen combustion engines require no expensive purification of hydrogen as FCV does¹⁷⁷. Actually, in the case of FCV, hydrogen must be purified to avoid Pt poisoning. Another benefit is that manufacturing of hydrogen combustion engines is independent from expensive materials i.e. Pt and fuel systems for FCV¹⁷⁸ and rare earth elements for BEV¹⁷⁷.

Nevertheless, some important shortcomings exist also for hydrogen combustion vehicles (HCV). Transportation and storage processes for hydrogen entail low “well-to-wheel” efficiency if hydrogen is produced from fossil fuels because much energy is required for its production. In addition, the difficulty of on-board hydrogen storage for HCV and FCV remains; current pressurized hydrogen systems are unsuitable in terms of efficiency¹⁷⁷. Actually, BEV has a better penetration rate than HCV and FCV today. This fact demonstrates that the use of hydrogen in the transportation sector still presents difficulty with current technologies.

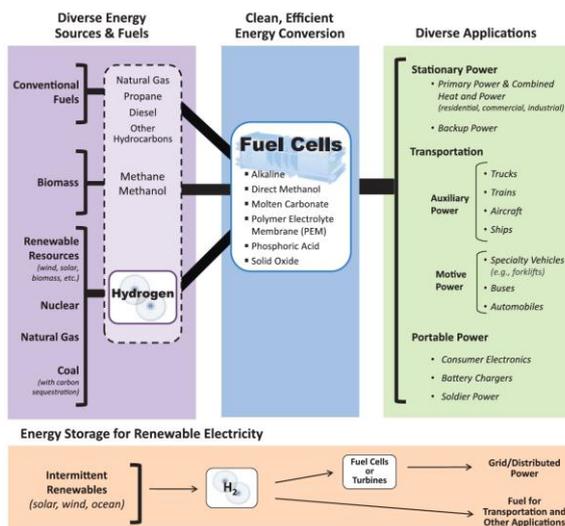
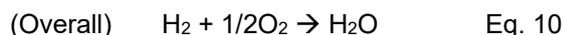
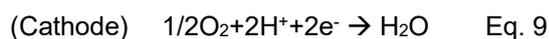
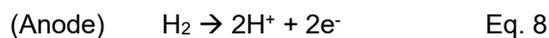


Figure 5 Fuel cell strategy by DOE (reprinted from DOE website).

5.2 Fuel cell

A fuel cell generates electricity from chemical energy through an electrochemical reaction of hydrogen fuel with oxygen. Fuel cells can achieve a decentralized power distribution system that is resistant to disasters of various kinds¹⁷⁹. Hydrogen is supplied to the fuel electrode (anode), and oxygen i.e. air to the air electrode (cathode)¹⁸⁰. The basic reactions at each electrode are represented as the following equations¹⁸⁰.



Fuel cells are classified according to the type of electrolyte and fuel. Operating temperatures and required fuel qualities differ by the type of fuel cell (e.g. proton electrolyte fuel cells, PEFC; phosphoric acid fuel cells, PAFC; molten carbonate fuel cells, MCFC; and solid oxide fuel cells, SOFC) ¹⁸⁰.

Because proton-conductive polymer such as Nafion requires highly humidified conditions, PEFC is commonly operated at temperatures below 373 K ^{181, 182}. At such low temperatures, Pt is used to facilitate the reaction at the anode electrode ¹⁸³. Consequently, expensive high-level purification of hydrogen fuel is necessary to eliminate carbon monoxide (CO). Recently, high-temperature PEFC (HT-PEFC) has been proposed, in which phosphoric acid (H_3PO_4) is used instead of water ¹⁸¹. Actually, HT-PEFC is operated at temperatures of 433–453 K resulting in higher carbon monoxide tolerance ¹⁸³. Operated at around 473 K, PAFC uses a solution of liquid H_3PO_4 acid ^{180, 184}. Therefore, PAFC presents similar benefits and shortcomings to those of HT-PEFC. Nevertheless, corrosion by liquid phosphoric acid remains difficult in the case of PAFC ¹⁸⁴. Actually, PEFC presents benefits for size reduction by virtue of its high-power density and tolerance of on–off switching because they are operated at lower temperatures than other fuel cells ¹⁸⁴.

Research efforts have demonstrated that MCFC and SOFC are operated at higher temperatures: 923 K for MCFC and 1073–1273 K for SOFC ¹⁸⁴. In MCFC, carbonate salts such as Li_2CO_3 - K_2CO_3 mixtures are used as electrolytes where carbonate salt conducts ^{180, 184, 185}. In SOFC, oxygen ion conducts through an electrolyte such

as yttrium-stabilized ZrO_2 (YSZ) ¹⁸⁶. Because both fuel cells are operated at high temperatures, hydrocarbons (e.g. methanol, methane) can be converted directly to hydrogen at the anode electrode with supported Ni ¹⁸⁶. Therefore, MCFC and SOFC are more applicable for centralized power generation with a co-generation system ¹⁸⁴.

6. Summary and future prospects

Based on the SDGs (sustainable development goals) and ESG (environmental, social, governance) investment, synthesis, transport and utilization of hydrogen is very important. Using water as a proton source for hydrogenation is also very promising considering the demand response to the renewable energy. Researches on solid state ionics, electrochemistry, and heterogeneous catalyst can bring a brighter future on the hydrogen synthesis, transport, and utilization.

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