Available online at www.sciencedirect.com
ScienceDirect
Focus Article, *Mendeleev Commun.*, 2014, **24**, 1–8
Mendeleev Communications

Hydrogen storage materials

Leonid M. Kustov,*[a] Andrei L. Tarasov,[a] Jae Sung[b] and Dmitry Yu. Godovsky[c,d]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: lmk@ioc.ac.ru*
[b] *Korea Institute of Energy Research, Yuseong-ku, Daejeon 305-343, Korea*
[c] *LG Chem Technical Center, 123610 Moscow, Russian Federation*
[d] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2013.12.001

Hydrogen storage materials including metal hydrides, carbon nanotubes, metal organic frameworks, and organic systems based on reversible hydrogenation–dehydrogenation cycles are compared in terms of the hydrogen storage capacity and the temperature required for storage and release of hydrogen.

Introduction

Hydrogen is considered a major energy resource for the future for ecologically friendly transportation vehicles. The problems and expenses associated with hydrogen storage, being compared with the low storage cost of gasoline, have prevented the use of hydrogen. Hydrogen can be a feasible alternative if the hydrogen storage problems are debottlenecked. Thus, a safe, compact and relatively light-weight hydrogen storage system is strongly required.

The storage material for hydrogen should possess such characteristics as (i) high hydrogen content (high energy density), (ii) rapid hydrogen supply (high power density), (iii) low storage energy consumption, (iv) economical performance/low cost and (v) safety. Several kinds of hydrogen storage media have been proposed and recently a few excellent review papers have been published.[1,2]

Among the hydrogen storage methods, the following options deserve most attention:

– use of compressed or liquefied hydrogen;
– adsorption by carbon nanotubes, fullerenes, zeolites, metal organic frameworks (MOF) and other adsorbents;
– reversible absorption (chemisorption) by intermetallides;
– decomposition of light metal hydrides with attempts to make these systems partially reversible;
– use of chemically bound hydrogen in aromatic substrates with consecutive cycles of hydrogenation and dehydrogenation of the saturated cyclic moieties;
– hydrogen contained in the ammonia molecule.

However, liquid hydrogen has proven unacceptable due to its cost/energy of liquifaction and requirements of a cryogenic storage temperature. Compressed gas is cheaper but requires high pressures and excessive storage space. Compressed hydrogen necessitates the development of special low-weight high-pressure vessels. Hydrogen absorption alloys have a fatal disadvantage in the hydrogen content, typically below 3.5 wt%, except for Mg_2Ni (5 wt%, but the temperature of hydrogen release is 570 K). The detailed overview of all available methods of hydrogen storage with adequate comparison and outline of drawbacks and advantages is presented in the review by Shashikala.[3]

The most promising methods of hydrogen storage are discussed in more detail. The compressed or liquid hydrogen is not described in this review in spite of some expectations of the efficient hydrogen storage systems based on tanks or cylinders made of composite multilayer materials for the compressed hydrogen up to about 60–80 MPa. The solution in the development of these approaches lies in the new high-pressure materials.

Professor Leonid M. Kustov is the head of the Laboratory of Development and Study of Polyfunctional Catalysts at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, and the head of the Laboratory of Ecological Chemistry at the Department of Chemistry, M. V. Lomonosov Moscow State University. He is an expert in the areas of physical chemistry, catalysis and petrochemistry. He has about 600 publications, including 30 reviews and 30 inventions.

Dr. Andrei L. Tarasov is Senior Research Fellow at the N. D. Zelinsky Institute of Organic Chemistry. He is a specialist in catalytic processes (hydrogenation, alkylation, partial oxidation, *etc.*), including microwave-assisted catalysis, as well as hydrogen storage.

Dr. Sung is a retired Senior Researcher at Korean Institute of Energy Research, Taejon, South Korea. He was also Director of Russia–Korea Research Center in Moscow in the period of 1995–2010. His interests extend from generation of hydrogen and energy to hydrogen storage and catalytic processes related to the energy sector.

Professor Dmitry Yu. Godovsky received his PhD degree in 1993 at Kurchatov Institute of Nuclear Energy where he worked for 10 years. In 1996–2003 he worked as a researcher in South Korea, Sweden and Germany. In 2011 he received his Dr. Sci. degree at the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, where he works now. His research interests are in polymer chemistry, energy conversion and storage, neural networks and conductive polymers.

Hydrogen storage by adsorption or absorption

Adsorption systems. Hydrogen storage by adsorption onto carbon materials at low temperatures or high pressures has been studied extensively,[4–6] though experimental reproducibility seems to be needed for the practical storage. Hirscher and coauthors[7] showed only a very low hydrogen storage capacity of about 1.0 wt% and concluded that the hydrogen storage capacity for carbon nanotubes cannot exceed 3.0 wt% at room temperature and high pressures up to 10 MPa. The nanodiamond material modified with Ni demonstrated about the same performance.[8] Somewhat better results were reported by Kim[9] who found an enhanced capacity of about 4.4 wt% for the Ni/graphite material at 298 K and 10 MPa. A system comprising a multi-wall carbon nanotube and a metal oxide catalyst somewhat enhances the hydrogen storage capacity.[10]

C_{60} fullerenes can serve as a hydrogen vehicle and be hydrogenated in the presence of a Pt-containing catalyst (such as Pt/SiO_2) to $C_{60}H_{18}$ or even to $C_{60}H_{36}$ structures.[11] Such systems may contain up to 5.0 wt% H_2 in the ultimate $C_{60}H_{36}$ product, but according to Talyzin and Jacob[12] the fullerene structure was partially destroyed because the hydrogenation in this system requires elevated temperatures. Analogous results were obtained using a Ru/C catalyst[13] that was capable of hydrogenating C_{60} fullerene into the $C_{60}H_{36}$ product with complete hydrogen release at 120 °C.

Thus, the figures presented in numerous publications on carbon nanotubes and carbon materials are far from the target set by Department of Energy of USA (DOE): 6.5 wt% H_2 at a temperature below 200 °C at 62 kg H_2 m^{-3} to provide a 350 mileage for a vehicle powered by a fuel cell,[14] in spite of some hopes expressed.[15] Note that both nanotubes and fullerenes are extremely expensive. In the best studied systems based on carbon nanotubes, the maximum capacity reaches 4.2 wt%. The main drawback of carbon nanotubes is the necessary use of cryogenic conditions.

New systems have been reported recently:[16,17] so-called metal organic frameworks (MOFs) prepared, for instance, from metal salts and carboxylic polyacids like terephthalates. One of the first known metal organic frameworks, MOF-5, $Zn_4O(bdc)_3$ (bdc = 1,4-benzenedicarboxylate) with a cubic three-dimensional extended porous structure adsorbed hydrogen up to 4.5 wt% (17.2 mol H_2 per formula unit) at 77 K and 1.0 wt% at room temperature and 20 bar. The MOF materials are characterized by the enhanced pore volume and adsorption capacity for many adsorbates including hydrogen. Nevertheless, the maximum hydrogen adsorption capacity reported for MOFs is in most cases around 4 wt% at 77 K and 1–1.5 wt% at room temperature.[18] MOFs with aluminum and chromium cations, possessing enhanced H_2 storage capacity have been also described.[19] These solids have H_2 storage capacities of 3.8 and 3.1 wt%, respectively, when loaded at 77 K under 1.6 MPa.

The best MOFs demonstrate excellent hydrogen storage capacity under the cryogenic high-pressure conditions (excess uptake of over 8 wt% at 5 MPa),[20] whereas at room temperature the hydrogen uptake is lower. However, systematic studies at high pressures are missing and an option of a high-pressure tank filled with MOF as an adsorbent is promising. The theoretical estimate of the highest possible H_2 storage capacity for covalent organic frameworks (COFs) is at the level of 20 wt%.[21] So, there are no principal constraints to reach the capacity of 6–7 wt% or higher at pressures in the range of 35–70 MPa. The tuning of the structure of MOFs/COFs by choosing appropriate organic linkers (di- or tricarboxylic acids) and the inorganic cations, as well as the synthetic approaches governing the formation of interwoven structures will turn efficient in reaching the capacity lead. The efficiency of the MOF materials may be enhanced by using loaded metals such as Li, Mg, Al and others.

Among the factors influencing the hydrogen storage efficiency, the following parameters should be mentioned:

– specific surface area;
– shape and size of the pores;
– availability of niches or side pockets;
– ratio of micro-to-meso porosity;
– presence of specific adsorption sites, like metal ions and atoms or NPs;
– presence of intergrown guest structures like calixarenes and dendrimers;
– possibility of formation of interwoven (two or more different MOFs) structures.

The role of the pore geometry can be illustrated by the high hydrogen adsorption capacity of MIL-53, based on benzenedicarboxylates [M(OH)(bdc) (M = Al^{3+}, Cr^{3+})].[22] The preparation with chromium showed the hydrogen adsorption capacity of *ca*. 3.1 wt%, and that with aluminum, *ca.* 3.8 wt% (77 K, 1.6 MPa).

One way to optimize the pore size in MOFs to match the size of the hydrogen molecule is creation of catenanes. A catenane structure is formed by 'fusion' of two or more identical frameworks, provided that the necessary free pore volume is available. The so-called 'catenation' can be in the form of interpenetration, when two or more identical frameworks are set as far apart as possible, or in the form of 'interweaving' when the distance between the frameworks is minimized and the latter are in close contact.[23] For instance, IRMOF-11 (4,5,9,10-tetrahydropyrene-2,7-dicarboxylate) is formed by two interwoven MOF structures. Although the pore volume usually decreases in this case, the narrow pores are formed that are capable of accommodating small H_2 molecules, especially if specific adsorption sites (metal ions and atoms) are present.

$Mn_3[(Mn_4Cl)_3(btt)_8(MeOH)_{10}]_2$ (btt = 1,3,5-benzenetristetrazol-5-yl) shows a total H_2 adsorption capacity of 6.9 wt% at 77 K and 90 bar and exhibits a maximum isosteric heat of adsorption of 10.1 kJ mol^{-1} among MOF materials.[22]

One of the currently most promising approaches to enhance the hydrogen adsorption capacity is the use of secondary hydrogen spillover.[24–26] The catalytic site (particle of metal) facilitates dissociation of hydrogen molecules into atoms, and monoatomic hydrogen 'spills over' across the surface towards the receptor. One currently used solution is the creation of carbon 'bridges', which are the result of carbonization of the surface[24] (Table 1).

The theoretical evaluation of MOFs as hydrogen storage materials predicts the optimal size of the pore to be about 0.7 nm, when exactly two layers of hydrogen molecules adsorb on opposite surfaces.[27] As for today, the highest reachable hydrogen capacities for MOFs are listed in Table 2.

The future research will be probably guided by the following hints to design the most efficient MOF-based hydrogen storage materials.

(i) The high surface area itself is a prerequisite, but, in general, there should be no linear correlation of the H_2 uptake and surface area at ambient temperatures (*cf*. example of carbon materials with surface areas up to 3000 m^2 g^{-1} but with a very low H_2 capacity, below 0.5 wt%).

(ii) The high pore volume is more important than the surface area, but again the overall pore volume does not reflect the pore distribution among micro/meso/macropores; for high H_2

Table 1 Spillover effect during hydrogen uptake (298 K, 10 MPa).[25]

Material	Surface area/ m^2 g^{-1}	H_2 uptake (wt%)
$Zn_4O(bdc)_3$ + 5% Pt/C/carbon bridges	3362	3.0
$Zn_4O(ndc)_3$[a] + 5% Pt/C/carbon bridges	1466	4.0

[a] ndc = naphthalenedicarboxylate.

Table 2 The best known results on H_2 storage on MOF materials.[a]

MOF	H_2 uptake		Conditions		Ref.
	wt%	g dm^{-3}	*T*/K	*P*/bar	
HKUST-1, MOF-199, $Cu_2(btc)_{1.33}$	3.6	22	77	10	28
$[Mn(DMF)_6]_3[(Mn_4Cl)_3(btt)_8(H_2O)_{12}]_2$	6.9	12.1	77 298	90	29
MOF-177, $Zn_4O(btb)_3$	7.5 11.3[b]	48.3[b]	77	60 70	30 29
MOF-646, $Zn_4O(adc)_3$		20.9	77	1	31
MOF-210, $Zn_4O(bte)(bpdc)$	8.6 2.9	44	77 298	80 100	19 26
MOF-200, $Zn_4O(bbc)_2$	7.4 3.2	36	77 298	80 100	19 26

[a]Abbreviations: btc = benzene-1,3,5-tricarboxylate; btb = benzene- 1,3,5-tribenzoate; adc = 1,3-azulenedicarboxylate; bte = 4,4′,4″-[benzene-1,3,5-triyltris(ethyne-2,1-diyl)tribenzoate]; bpdc = biphenyldicarboxylate; bbc = = 4,4′,4″-[benzene-1,3,5-triyltris(benzene-4,1-diyl)tribenzoate]. [b]Absolute predicted value of the adsorbed amount.

capacities, we need more micropores, less mesopores and no macropores at all.

(iii) The synthesis should be directed towards the formation of intergrown (or interwoven, or catenated) MOF structures, *i.e.*, two or more MOF architectures built-in each other.

(iv) The use of other guest structures with nanopores or nanocavities, like calixarenes or 1st or 2nd generation dendrimers built in the MOF structure, especially in the interwoven structures, will certainly enhance the H_2 uptake.

(v) The encapsulation of light metals inside the nanopores or nanocavities of MOFs or inside the calixarene baskets, or inside the branches of the dendrimer will result in the hydrogen spillover and further enhancement of the H_2 capacity.

(vi) The use of functional groups at the organic linkers forming the MOF/COF structure (for instance, NH_2) will increase the hydrogen adsorption capacity.

(vii) Finally, all the approaches sketched above do not result in any high heats of hydrogen adsorption, which are typically not higher than 10 kJ mol^{-1}, thus excluding the necessity of heat exchangers in gas tanks filled with MOF.

Except MOFs, similar systems called microporous metal coordination materials (MMCMs) were studied.[32] For these materials, the pore dimensions are comparable to the size of molecular hydrogen. MMCMs share characteristics of single-wall carbon nanotubes (SWCNTs), *i.e.*, both are lightweight and composed of open channels based on aromatic carbon. However, MMCMs possess several promising advantages, *i.e.*, they can incorporate hydrogen-binding metals, while the interactions with H_2 can be enhanced by modification of the organic component, and the open channels are perfectly ordered for effective access of hydrogen. One of such materials, $Cu(hfipdb)(H_2hfipdb)_{0.5}$ [hfipdb = 4,4′-(hexafluoroisopropylene)dibenzoic acid], was synthesized and characterized.[32] The hydrogen uptake was compared with that of SWCNTs and MOF-5. The hydrogen storage capacity was 1.65 wt% at 300 K and 48 bar. Although the accessible volume of MOF-5 is about 6.6 times larger than that of the new MMCM, the factor for the hydrogen uptake is not higher than 1.8, and the hydrogen volume density in the MMCM is much higher than those in MOF-5. Thus, the correspondence of the pore size to the H_2 molecular diameter may be a basis to approach the DOE target of 0.036 g H^2 cm^{-3} for the year 2005 at medium pressures.

Light metal hydrides and intermetallides. This type of absorption materials is most comprehensively studied and includes various patented metal hydrides, which can be irreversible like $NaBH_4$, $LiAlH_4$, and AlH_3, or reversible, such as $LaNi_5$, Mg_2Ni, *etc*. Several types of such hydrogen storage materials are presently known, some of them being quite reliable and cheap, others being sophisticated and irreproducible as well as expensive. The hydrogen storage capacities for such systems are in the range from ~0.5–3.5 wt% (reversible systems) to about 10–12 wt% (irreversible systems), although the maximum level is hardly reachable because of the need to use solvents in the latter case. Some of the irreversible systems were introduced on a commercial scene, such as the Millenium $NaBH_4$ system based on the hydrolysis of sodium borohydride. These systems provide rather high hydrogen storage capacity (theoretically, 10–11%, but since they are used in solutions, the real H_2 storage capacity does not exceed 5 wt%) and the consumed material ($NaBO_2$) should be recovered; thus, these systems are very expensive. The reversible metal hydrides (intermetallides such as $LaNi_5$ or Mg_2Ni) are much cheaper.

Other light metal hydrides (MgH_2, AlH_3, $LiAlH_4$) are developed to a lesser extent, but further disadvantages of safety may limit their use. The MgH_2–Mg system[33] or a Mg-rich Mg–Ni alloy is the most appropriate of all known metal–hydride and metal systems that can be used as reversible hydrogen storage systems because it has the highest capacity (7.65 wt% for MgH_2 and ~5 wt% for Mg_2Ni) of reversibly bound hydrogen and hence the highest energy density (2.332 kWh kg^{-1}). However, the release of hydrogen requires the use of rather high temperatures (~300 °C). For intermetallides the hydrogen capacity may be increased to 4.0 wt%.[34]

Various metal alloys, such as $LaNi_{4.8}Mn_{0.2}$[35], which is conventionally difficult to use because of a low equilibrium hydrogen pressure, were tested in hydrogen storage containers. While some progress has been achieved by using metal hydrides for hydrogen storage in automobiles, the resulting storage tank is prohibitively heavy, thereby resulting in reduced driving ranges. Additionally, the most efficient metal hydrides must be heated to temperatures higher than 300 °C before the bonded hydrogen is released, which further limits the effectiveness of the system.

The $La_2Mg_{16}Ni$ alloy prepared by mechanical ball milling in benzene under argon exhibited improved hydrogen uptake.[36] The hydrogen storage material based on magnesium alloy powder containing about 90 wt% Mg[37] was found to have (i) a hydrogen storage capacity of about 5 wt% and (ii) absorption kinetics such that the alloy powder absorbs 80% of its total capacity within 5 min at 300 °C. Modifiers added to the magnesium to produce the alloys include Ni, Mm (mischmetal) and additional elements such as Al, Y, and Si.

The layered deformation structure obtained when a starting material is subjected to plastic deformation was shown to be beneficial for the improved performance in hydrogen storage.[38] Hydrogen in such systems is trapped in the defect sites, resulting in the improved hydrogen storage capability. Moreover, since the defect sites serve as a fast hydrogen diffusion path, formation of the defects at a high density significantly reduces the hydrogen desorption temperature.

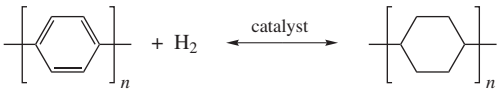
Catalytically enhanced hydrogen storage systems were also described.[39,40] These systems are based on the reversible reaction $3\,NaAlH_4 \leftrightarrow Na_3AlH_6 + 2\,Al + 3\,H_2$, occurring in the presence of a catalyst such as $TiCl_3$. The maximum hydrogen uptake for this system was found to be 4.4 wt% at 120 °C and very high hydrogen pressure of 125 atm.[41] The effects of two types of dopants on the rates of the dehydrogenation of doped $NaAlH_4$ to Na_3AlH_6 and Al were studied under the practical conditions of 100 °C and 1 atm. Aluminum–transition metal alloys (*e.g.*, TiAl, Ti_3Al, Zr_3Al, and Ni_3Al) had little or no effect, whereas doping with transition metal–aluminum hydride complexes resulted in only modest kinetic enhancement. The dehydrogenation rates of hydride doped with 2 mol% $Ti(OBu)_4$ or $TiCl_3$ were adequate to meet the demands of a fuel cell operating under practical

conditions. Mixtures of NaH and Al doped with 2 mol% $Zr(OPr)_4$ undergo hydrogenation to $NaAlH_4$ in 15 min under 120 atm of hydrogen pressure at 120 °C. Solid-state ^1H NMR spectroscopy has shown that ~25% of hydrogen in $NaAlH_4$ is highly mobile at ambient temperature and titanium doping significantly increases the proportion of mobile hydrogen in the bulk material. ^{27}Al and ^{23}Na NMR studies indicated that the mobility of hydrogen results from the breaking of Na–H rather than Al–H bonds.

Hydrogenation/dehydrogenation of aromatic substrates

A new approach to hydrogen storage may be based on reversible hydrogenation–dehydrogenation of aromatic and heterocyclic compounds. In general, the use of oil and other hydrocarbons, such as benzene, cyclohexane, decalin, *etc*., *via* catalytic dehydrogenation for production of hydrogen was summarized.[42]

The use of composite materials including a catalyst and an aromatic compound capable of functioning in hydrogenation–dehydrogenation mode gives the key to design new efficient systems for hydrogen storage.



Such reversible catalytic reaction pairs as methylcyclohexane dehydrogenation–toluene hydrogenation were proposed earlier. In 1995–2000, Ir-containing pincer homogeneous catalysts were developed for hydrocarbon (benzene) hydrogenation–dehydrogenation cycles.[43] The $IrH_2[C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2]$ was shown to be the best catalytic system for the above reversible reactions.[44,45] The disadvantages of this system are the high cost of the catalyst, partial loss of the hydrocarbon during the process and deactivation of the catalyst. The arsino pincer complex, $IrH_2[C_6H_3\text{-}2,6\text{-}(CH_2AsBu^t_2)_2]$ was also synthesized and tested in the dehydrogenation of methylcyclohexane to toluene. The conversion >20% was obtained with this catalyst, which was much greater than the 10% conversion obtained using $IrH_2[C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2]$, but far from the practically significant conversion >90%.

The use of such homogeneous catalysts in the hydrogen storage materials based on reversible cycles of hydrogenation–dehydrogenation using a reaction chamber equipped with a selective membrane was published.[46] The storage/release system is lightweight, low-cost, recyclable and does not have a prohibitively high or low operating temperature. The system operates at 150 °C, but the conversions are typically low.

Polynuclear organometallic compounds[47] shown below can be used as the catalysts for reversible dehydrogenation. They comprise a tripodal pincer ligand containing an aromatic ring and neutral Lewis bases indirectly linked to the aromatic ring (M, M′ = Rh, Ru, Ir, Os, Fe).

For these complexes, such pairs as fullerenes–hydrofullerenes were even proposed for the reversible hydrogenation–dehydrogenation process,[48] which has already been mentioned above.

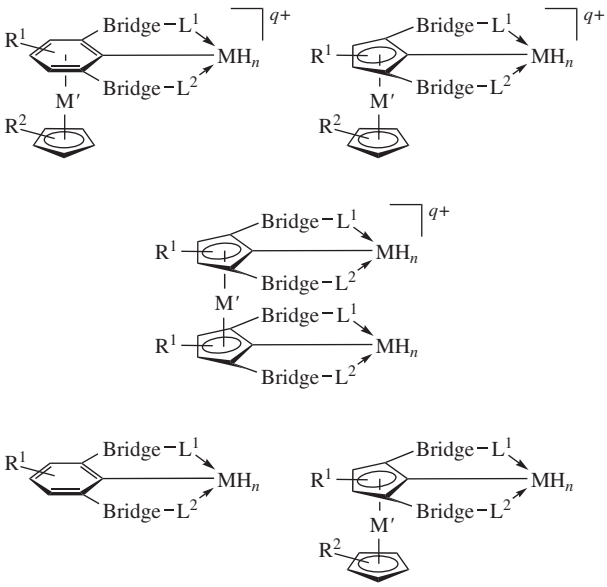
There are numerous publications and patents on the hydrogen storage through the reversible hydrogenation of aromatic hydrocarbons and dehydrogenation of their hydrogenated counterparts (naphthenes) on the heterogeneous catalysts. These catalysts showed some advantages over the homogeneous systems:

– the heterogeneous catalysts are much cheaper;

– they can be easily recycled and regenerated (in the case of deactivation);

– the heterogeneous catalyst systems allow one to use diverse and economic option for the design of the hydrogen storage unit.

Nevertheless, the heterogeneous systems are well known to be somewhat inferior to the homogeneous catalysts in terms of the activity.



As for design of the hydrogen storage, the hydrogenation–dehydrogenation processes are typically based on decaline–naphthalene interconversion.[49] This pair looks attractive because of the liquid state of decaline at room temperature, but has a disadvantage of continuous losses of the substrates during the dehydrogenation–hydrogenation cycles. The losses of the liquid substrate are explained not only by the high vapour pressure under the dehydrogenation conditions (typically above 200–250 °C), but also by the increasing possibility of the occurrence of side reactions during the repeated cycles with the substrate molecule. The most important side reactions are considered as following:

– cracking, ring opening, or hydrocracking (hydrogenolysis) of the aromatic hydrocarbons during the hydrogenation–dehydrogenation cycles, which convert aromatics to light products or ring-opened products that are lower-boiling hydrocarbons and thus tend to leave the system with hydrogen; this results in irreversible loss of the H_2 storage capacity;

– formation of strongly condensable hydrocarbons, such as formation of tars and coke which turn the substrate into a solid material that cannot be removed easily from the reaction volume; these heavy products can also deactivate the homogeneous or heterogeneous catalysts.

Among the substrates described in the literature, the most studied ones are (let us discuss the dehydrogenated counterparts): benzene,[50] toluene,[51] naphthalene,[52,53] methylnaphthalene,[54] biphenyl[55] and other condensed aromatics, as well as some heterocyclic molecules. With biphenyl, the alloy catalyst $MmNi_{3.5}Co_{0.7}Al_{0.8}H_{4.2}$ [Mm is the mischmetal, the mixture of La, Ce, Pr, and Nd (30 : 52 : 5 : 13, by weight)] gave either cyclohexylbenzene or bicyclohexyl. Selective hydrogenation was observed with such aromatic compounds as biphenyl and 2-phenylpyridine.[56]

Newson *et al*.[57] reported decalin dehydrogenation using the heterogeneous catalysts at 440 °C. In the case of toluene,[58] the stability of the Pt–Sn–K/Al_2O_3 catalyst was shown to be at least 8 times higher than that of an industrial catalyst under the reaction conditions of 400 °C, weight hourly space velocity of 6 h^{-1}, atmospheric pressure, pure methylcyclohexane feed. However, the low-temperature activity of the modified catalyst needs to be further improved. The hydrogen storage capacity is 2.78–6.12 wt% at 300–400 °C. Loutfy *et al*.[59] adopted the membrane reactor for catalytic decalin dehydrogenation at moderate temperatures (260–320 °C) to avoid thermodynamic limitations.

In 'liquid-film concept', implying the use of reactive distillation conditions when the liquid substrate to be dehydrogenated

forms a thin liquid film, carbon-supported platinum-based catalysts were used for hydrogen evolution from decalin at 200–300 °C. Pt/C catalysts were proposed for decalin dehydrogenation using the 'liquid-film concept' as an approach to new hydrogen storage materials.[61,62] The same authors described this process in the superheated liquid-film state.[63] A coupled process of catalytic decalin dehydrogenation and subsequent naphthalene hydrogenation has been proposed as a hydrogen source for fuel-cell vehicles; 24.6% of per-path conversion at 210 °C was attained due to superheated catalytic active sites. In order to evolve hydrogen from decalin efficiently under mild conditions, its catalytic dehydrogenation in a liquid-film type reactor was achieved with carbon-supported platinum-based fine particles under reactive distillation conditions.[64,65] The catalyst layer was superheated in the liquid-film state, which gave much higher hydrogen evolution rates and higher conversions at 210 °C than those in the suspended state. Carbon-supported bimetallic catalysts (Pt–W/C or Pt–Re/C) gave much larger conversions and reaction rates at the range of temperatures of 210–280 °C. The state of platinum was shown to have a crucial influence on the catalyst performance.[66] The liquid-film concept was confirmed to be effective for practical operation because of its sufficient power densities in addition to its higher hydrogen contents (7.3 wt%, 64.8 kg H_2 per m^3) than the DOE target values (6.5 wt%, 62.0 kg H_2 per m^3). Requirements concerning high evolution rates of hydrogen or high power densities for practical fuel-cell vehicles would be fulfilled enough at around 280 °C. However, as in the case of the homogeneous systems, the reaction temperatures are rather high and the selectivity to target products is lower than the economically viable figures. Evaporation loss during storage is not significant (but still not negligible) because of the high boiling points of the hydrogenated and dehydrogenated substrate: 187 °C (*trans*-decalin), 196 °C (*cis*-decalin) and 218 °C (naphthalene). Both of decalin isomers and naphthalene are socially accepted as safe commodity chemicals (solvents and insect killers). Naphthalene is thixotropic and easy to change into an oily state with a small amount of hydrocarbon additives. Widely distributed gas stations and tank lorries are available for storage and transportation of the naphthalene oil. Since 1940s, commercial catalytic naphthalene hydrogenation had been introduced.

In the portable storage system based on the decalin/naphthalene pair, therefore, efficient catalytic hydrogen evolution from decalin under mild conditions can be achieved.[67]

A few more patents have been filed in 2003–2004 covering the hydrogenation–dehydrogenation of aromatic molecules in hydrogen storage. Processes are provided for the storage and release of hydrogen by reversible catalytic hydrogenation of extended π-conjugated substrates which include mostly large condensed polycyclic aromatic hydrocarbons, condensed aromatic hydrocarbons with nitrogen or oxygen heteroatoms, polycyclic aromatic hydrocarbons with alkyl, alkoxy, ketone, ether or polyether substituents, π-conjugated molecules comprising five-membered rings, six- and five-membered rings with nitrogen or oxygen heteroatoms, and extended π-conjugated organic polymers containing condensed aromatic moieties and heterocycles.[68] The conjugated substrates can be pyrene, perylene, chrysene, triphenylene, coronene, hexabenzocoronene, ovalene, picene, rubicene, fluorene, indene, acenaphthylene, carbazole, 1,4,5,8,9,12-hexaazatriphenylene, phenanthroline, quinoline, acridine, dibenzofuran, polypyrrole, polyindole, poly(methylcarbazole), polyacenaphthylene, polyaniline, polyindene, and poly(9-vinylcarbazole). The hydrogenation and dehydrogenation catalysts include supported Ti, Zr, Co, Nb, Ta, Fe, Mo, W, Ru, Rh, Ir, Ni, Pd, or Pt. The catalyst can be supported on silica–alumina, alumina, zeolites, sulfonated zirconia, solid perfluorinated polymeric sulfonic acids, AlF_3, aluminum chlorofluorides, $ZnCl_2$, $AlCl_3$, $SnCl_4$, copper trifluoromethane sulfonate, $ScCl_3$, or hexafluoro acetylacetonate complexes of lanthanide elements. The hydrogen contained in the partially hydrogenated form of the extended π-conjugated system can be released by a catalytic dehydrogenation in the presence of a catalyst which can be affected by raising the temperature to 200–250 °C. However, the dehydrogenation reactions were carried out at a rather low conversion of the saturated substrates into the unsaturated counterparts and the 100% conversion corresponding to ~6–7 wt% hydrogen storage capacity was not achieved. This can be explained by the occurrence of intense side reactions of heterocyclic molecules leading to condensed products, Schiff bases and other products, thereby reducing the reproducibility and reversibility of the process.

Note that the poor selectivity at the dehydrogenation step is a general disadvantage of all reported systems used in aromatics hydrogenation–dehydrogenation cycles. This is caused by the ring opening, hydrocracking, hydrogenolysis, and coke formation reactions leading to a decrease in the catalyst activity and a loss of the aromatic substrate because of the gaseous products formation.

Decalin dehydrogenation is highly endothermic (ΔH = = +297.3 kJ mol^{-1} at 298 K) and thermodynamically restricted at low temperatures.[69] The conventional heterogeneous catalysis of dehydrogenation in the solid–gas phase is therefore performed at temperatures over 300 °C, which might result in the formation of by-products or carbonaceous deposit over the catalyst in addition to thermal energy loss.

There are a few more examples of using different materials as catalysts in hydrogen storage units, *i.e.*, hydrogenation of several aromatic compounds was conducted using the activated hydrogen storage alloys such as $LaNi_5$ with a crystal structure of a hexagonal crystal or $MmNi_{3.5}Co_{0.7}Al_{0.8}H_4$ at a relatively high temperature (160–240 °C) under nitrogen atmosphere.[71] Another system comprises a bimetallic catalyst providing a better performance.[72] Some other, more complicated catalysts like Pt–Sn bimetallic composition additionally modified with alkaline metals were also proposed to improve the selectivity.[73] A nanocomposite zeolite catalyst was reported for the benzene conversion.[74] Ni–Ce nanoparticles were prepared by H_2 plasma treatment. The catalytic activity of 5A zeolite-supported Ni–Ce nanoparticle catalyst for gas-phase hydrogenation of benzene was related to the H_2 storage and the existence of Ni–Ce alloy on the surface layer. The supported catalyst showed high selectivity for cyclohexane and high stability in benzene hydrogenation.

A Pt–W/C catalyst also demonstrated good performance in decaline dehydrogenation.[75] This system was investigated under mild reaction conditions (200–210 °C, 1 atm) and was found to be active for hydrogen evolution from decalin to naphthalene under reflux conditions.

Hydrogenation of naphthalene can be carried out even in the presence of sulfur compounds (~50 ppm) that are at most present in hydrocarbons produced from oil fractions.[76,77] For this purpose, sulfur-tolerant catalysts have been developed, some of them keep activity at extremely high concentrations of sulfur in the feed (up to 1000 ppm).[78]

A combination of two approaches (the use of intermetallides and the reversible hydrogenation–dehydrogenation of aromatic substrates) was proposed.[79]

A similar approach to hydrogen storage was invented, which is based on the use of highly selective and efficient catalytic composite materials for hydrogen storage.[80] These materials are the composite of an unsaturated hydrocarbon (terphenyl and polyphenylenes were basically used) that is different from the earlier reported and described in the available patents, such as naphthalene, light aromatics or heavy condensed aromatics or heterocycles. Another distinctive feature of the new system is

the application of a very selective hydrogenation/dehydrogenation nanocatalyst. The materials can be used repeatedly without the losses of activity and noticeable hydrogen storage capacity. They are cheaper and the ingredients of the composites are available on the market. The maximum hydrogen storage capacity reached for these composites is ~8.0 wt%. Under cryogenic starting conditions the capacity can be increased to about 9–10%. New efficient catalysts for hydrogenation of aromatics such as naphthalenes, terphenyls and aromatic polymers such as polystyrenes and dehydrogenation of the corresponding cyclic moieties on the basis of conventional and specially designed oxide systems, such as mesoporous SiO_2, mixed oxides, or modified (oxidized) carbon carriers were found. These catalysts provide enhanced activity in the hydrogenation of the aromatic compounds (typically the rate constants are 2–3 times higher as compared to conventional Pt/Silica or Pt/activated carbon systems), as well as in the reverse dehydrogenation reaction so that no side reactions like cracking, hydrogenolysis, ring opening, or coke formation occur on the new catalysts. The key in creating such efficient systems is the proper design of the carrier and the control of the dispersion of metal nanoparticles and their interaction with the carrier surface.

The application of various micro- and mesoporous oxide materials with surface areas up to 1000 $m^2\ g^{-1}$ may also be efficient in designing new hydrogen storage materials. Of particular interest are the systems prepared by sol–gel technique and under supercritical conditions, because they provide unique pore size distribution and enhanced surface areas. The modification and use of various carbon-based materials with significant surface areas is another way to enhance the performance of the catalysts. Thus, partial oxidation of the surface of carbon carriers allows one to reach extremely high dispersion of the supported metals and their stability toward sintering as well as enhanced activity in the hydrogenation/dehydrogenation cycles. The use of a Pd-membrane or microwave heating in the terphenyl/tercyclohexyl hydrogenation/dehydrogenation reactor may be helpful for decreasing the dehydrogenation temperature to below 200 °C. Other methods can also be employed for decreasing the dehydrogenation temperature and thus enhancing the energetic efficiency of the process. The performances of the new systems in comparison with the available hydrogen storage systems (carbon nanotubes, intermetalides, MOFs, *etc*.) are presented in Table 3. Note that the developed method of hydrogen storage is extremely safe because, unlike carbon nanotubes and metal hydrides, hydrogen is preserved in the chemically bonded state, *i.e.*, is inflammable and unexplosive. The new approach differs from the other works on reversible hydrogenation–dehydrogenation by using (i) a high boiling point substrate when reactive distillation and liquid-film conditions are not necessary and (ii) extremely selective and active catalyst characterized by the selectivity in both hydrogenation and dehydrogenation steps of 100%.

Table 3 Comparison of new H_2 storage systems with intermetalide and carbon systems.

Material	Advantages	Disadvantages
SWCNTs	Rather high capacity (~4.2 wt%) Lightweight	High pressure Very expensive Limited production Cryogenic (adsorption) Fast H_2 release Irreproducibility
Intermetalides	Available production Control of H_2 release	Expensive Heavyweight Irreversible Low capacity (3.5 wt%)
MOFs	High pore volume Control of H_2 release Lightweight	Expensive Commercially unavailable Low capacity (2.0 wt%)
Hydrogenation/ dehydrogenation on catalyst composites	Main components are available on the market Extremely high capacity (~8 wt%, up to 10 wt%) Non-cryogenic Control of H_2 release Fast reloading (15 min) Low pressure (5–20 atm)	High temperature H_2 release (250–300 °C) which may be decreased to 200 °C by using microwave heating

Table 4 Hydrogen content and energy consumed for portable storage of hydrogen.

Hydrogen medium	Hydrogen content		Energy consumption/ kWh $(kg\ H_2)^{-1}$
	wt%	$\times 10^{28}$ H atom m^{-3}	
Liquid H_2	100	4.2	10–14[a]
Compressed H_2	100	2.8	2.6[b]
$LaNi_5H_6$	1.4	6.2	0.32[c] (50 °C)
Terphenyl	7.5	4.5	0.43[c] (320 °C)

[a] Mechanical energy required for liquefaction. [b] Mechanical energy required for compression (~15% of hydrogen capacity at 70 MPa, ambient temperature). [c] Energy consumption calculated from $\Delta G = (1 - T_0/T)\Delta H$ (T_0 is the ambient temperature, ΔH is the heat of reaction); 0.278 kWh = 1000 kJ.

In the presence of the commercially available hydrogenation catalysts, the endothermic catalytic reaction of tercyclohexyl dehydrogenation was now performed at 280 °C (modified carbon-supported platinum-based catalysts). Under liquid conditions, hydrogen was evolved from tercyclohexyl much more efficiently than in the case of the suspended system.

The major problem of the hydrogen storage systems based on reversible hydrogenation–dehydrogenation cycles is the use of the heat of the exothermic reaction; the system is capable of attaining rather high values of the H_2 storage capacity (1 kg terphenyl + + 50 g of the catalyst) and can theoretically accumulate 39.0 mol (875.3 dm^3) of hydrogen (7.5 wt%) as the result of full selective aromatic substrate hydrogenation: $C_{18}H_{14} + 9H_2 = C_{18}H_{32}$.

During the charging stage, the exothermal reaction with heat production occurs fast, therefore, at this stage it is only necessary to warm up the system until the beginning of the reaction to reach the operating temperature in the autothermal regime. The heat effect for the charging stage is about 828 kJ kg^{-1}.

i) The heat consumed on heating the system up to the temperature necessary for the charging stage (180 °C) is 266.8 kJ kg^{-1}.

ii) The heat consumed on heating the system up to the temperature necessary for hydrogen evolution (320 °C) is 676.8 kJ kg^{-1}.

iii) The sum of the heats consumed on heating and operating of the system during one complete cycle is 943.6 kJ kg^{-1}, *i.e.*, it exceeds the heat effect of the chemical reaction during the charging stage by 115.6 kJ kg^{-1}.

Such a thermal energy from the outside is needed for the stable operation of the system. One kilogramm of the hydrogen storage system is capable to keep about 75 g of hydrogen (37.5 mol). The heat effect of hydrogen combustion ($2H_2 + O_2 = 2H_2O$) is 285.9 kJ mol^{-1}. So, the combustion of ~0.4 mol of hydrogen (~1.1% of the H_2 amount in the system) will provide 115.6 kJ of heat indispensable to heating the system during both stages. The calculations were made without taking into account the thermal losses. An input to a system of any heat source is possible, for example the heat of exhausts of motor engines. Thus, it is a problem to be solved how to utilize the heat released at the hydrogenation step. Comparison of available hydrogen storage methods with the new system is given in Table 4.

Thus, the main advantages of the new hydrogen storage composite systems in comparison with the available hydrogen storage systems (SWCNTs, intermetalides, MOFs, *etc*.) are as follows:

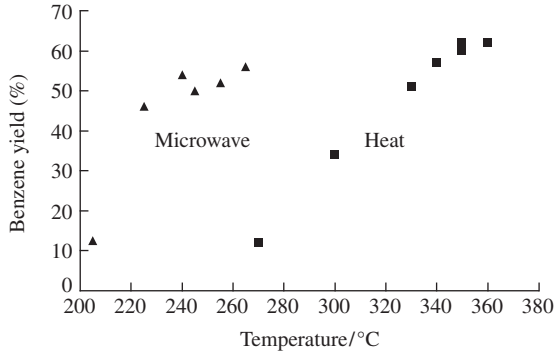


Figure 1 Effect of the power of microwave irradiation on the catalyst activity in cyclohexane dehydrogenation.[82]

(i) more efficient (7–8 wt% H_2, up to 9–10 wt%);

(ii) cheaper (5–10 times) and lesser weight than known systems based on SWCNTs, irreversible hydrides and intermetalides;

(iii) completely reusable and reversible;

(iv) short time (15 min) and low pressures (5–20 atm) of charging.

Microwave irradiation can be used to provide energy for heating of substrates and catalysts of the hydrogen storage systems. While exploring microwave-assisted catalytic processes of hydrogenation–dehydrogenation of various substrates and homogeneous metal complex catalysts, the following conclusions were drawn: (i) the dehydrogenation temperature can be substantially decreased from 280–320 °C to 150–200 °C if the catalytic process is performed under the microwave activation, (ii) some metal complexes show enhanced dehydrogenating activity towards aromatic substrates thus allowing to diminish the temperature of the dehydrogenation stage in the reversible cycles of hydrogen storage. Microwave activation does not affect the thermodynamics of the dehydrogenation process and the observed decreased temperature of the dehydrogenation reaction measured by the optical pyrometer gage is the averaged temperature of the catalyst surface, with the metal nanoparticles being the centers of the microwave energy absorption heated up to the desirable 300–350 °C for the dehydrogenation to occur. However, the insulated material of the carrier is not heated, thus allowing for the tremendous decrease of the energy consumption.

The treatment of catalysts by microwave radiation was found to be most effective technique affecting the activity and other properties of catalysts based on carriers that can absorb microwave radiation, for example, titania and carbon supports. It was shown that there are some optimal values of the microwave power that result in a multiple increase (3–5-fold) in the activity of the catalysts in the hydrogenation of aromatic hydrocarbons.[82,83]

Figure 1 shows the yield of benzene from cyclohexane as a function of the reaction temperature for a microwave-treated 1% Pd/TiO_2 catalyst in comparison with the thermal process. These data unambiguously support the efficiency of nontraditional treatments of heterogeneous catalysts on the catalytic properties.

Conclusions

The development of new methods and materials for hydrogen storage proceeds in several parallel directions, with metal organic frameworks and dehydrogenation of liquid organic substrates being most efficient and providing the H_2 storage capacity of at least 6 wt%. The combination of different materials and approaches (a hybrid system) may turn out to be more efficient than the use of a single material. Application of nontraditional approaches such as microwave activation or electroconductivity heating may improve the performance of the systems.

This work was supported by the Ministry of Science and Education of the Russian Federation (agreement nos. 8431 and 8441 between the Ministry, N. D. Zelinsky Institute of Organic Chemistry and the Russian Academy of Sciences).

References

1 P. Jena, *J. Phys. Chem. Lett*., 2011, 206.
2 J. Graetz, J. J. Reilly, V. A. Yartys, J. P. Maehlen, B. M. Bulychev, V. E. Antonov, B. P. Tarasov and I. E. Gabis, *J. Alloys Compd.*, 2011, **509S**, S517.
3 K. Shashikala, in *Functional Materials: Preparation, Processing and Applications*, eds. S. Banerjee and A. K. Tyagi, Elsevier, 2012, pp. 607–637.
4 W. Zhao, V. Fierro, C. Zlotea, E. Aylon, M. T. Izquierdo, M. Latroche and A. Celzard, *Int. J. Hydrogen Energy*, 2011, **36**, 11746.
5 P. Benard and R. Chahine, *Int. J. Hydrogen Energy*, 2001, **26**, 849.
6 B. K. Gupta and O. N. Srivastava, *Int. J. Hydrogen Energy*, 2001, **26**, 857.
7 M. Hirscher, M. Becher, M. haluska, U. Dettlaff-Weglikowska, A. Quintel, G. S. Duesberg, Y.-M. Choi, P. Dwones, M. Hulan, S. Roth, I. Stepanek and P. Bernier, *Appl. Phys*., 2001, **A72**, 129.
8 E. A. Tveritinova, Yu. N. Zhitnev, I. I. Kulakova, A. N. Kharlanov, N. B. Cherkasov, S. V. Savilov and V. V. Lunin, *Mendeleev Commun*., 2013, **23**, 249.
9 B.-J. Kim and S.-J. Park, *Int. J. Hydrogen Energy*, 2011, **36**, 648.
10 A. Lueking and R. T. Yang, *J. Catal*., 2002, **206**, 165.
11 V. Ya. Davydov, N. Sheppard and E. Osawa, *J. Catal*., 2002, **211**, 42.
12 A. V. Talyzin and A. Jacob, *J. Alloys Compd*., 2005, **395**, 154.
13 K. K. Tae, K. I. Sung and K. C. Young, *Jpn. Patent 0527080 A*, 1993 (*Chem. Abstr*., 1994, **91**, 52587).
14 L. E. Klebanoff and J. O. Keller, *Int. J. Hydrogen Energy*, 2013, **38**, 4533.
15 D. V. Schur, B. P. Tarasov, S. Yu. Zaginaichenko, V. K. Pishuk, T. N. Veziroglu, Yu. M. Shul'ga, A. G. Dubovoi, N. S. Anikina, A. P. Pomytkin and A. D. Zolotarenko, *Int. J. Hydrogen Energy*, 2002, **27**, 1063.
16 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127.
17 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
18 O. M. Yaghi, *Abstracts of Papers, Proc. 228th ACS National Meeting*, Philadelphia, USA, 2004, FUEL-193.
19 G. Ferey, M. Latroche, C. Serre, F. Millange, T. Loiseau and A. Percheron-Guégan, *Chem. Commun.*, 2003, **24**, 2976.
20 H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.
21 E. Tylianakis, E. Klontzasa and G. E. Froudakis, *Nanoscale*, 2011, **3**, 856.
22 S. Aguado, Ch.-H. Nicolas and V. Moizan-Baslé, *New J. Chem*., 2011, **35**, 41.
23 S. R. Batten and R. Robsom, *Angew. Chem. Int. Ed*., 1998, **37**, 1460.
24 F. H. Yang and R. T. Yang, *Carbon*, 2002, **40**, 437.
25 A. J. Lachawiec, G. S. Qi and R. T. Yang, *Langmuir*, 2005, **21**, 11418.
26 Y. Li and R. T. Yang, *J. Am. Chem. Soc*., 2006, **128**, 8136.
27 L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev*., 2009, **38**, 1294.
28 J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc*., 2006, **128**, 1304.
29 M. Dinca and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172.
30 H. Furukawa, M. A. Miller and O. M. Yaghi, *J. Mater. Chem.*, 2007, **17**, 197.
31 S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O. M. Yaghi and H. Berke, *Chem. Commun.*, 2010, **46**, 7981.
32 L. Pan, M. B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath and J. K. Johnson, *J. Am. Chem. Soc*., 2004, **126**, 1308.
33 B. Bogdanovich, *US Patent 5,199,972 A*, 1993 (*Chem. Abstr*., 1994, **101**, 133325).
34 S. S. Mao, S. Shen and L. Guo, *Prog. Nat. Sci.: Mater. Int.*, 2012, **22**, 522.
35 N. Kouichi and S. Kouichi, *US Patent 5,987,895 A*, 1999 (*Chem. Abstr*., 2000, **129**, 327920).
36 H. Chi, C. Chen, L. Chen, Y. An and Q. Wang, *Int. J. Hydrogen Energy*, 2004, **29**, 737.
37 S. R. Ovchinsky and R. Young, *US Patent 6,305,442 B1*, 2001 (*Chem. Abstr*., 2001, **134**, 165730).
38 K. Nozomu and S. Kouichi, *US Patent 6,329,076 B1*, 2001 (*Chem. Abstr*., 2001, **134**, 119305).
39 C. M. Jensen, *Proc. of 2001 US DOE Hydrogen Program Review*, Baltimore, USA, 2001, NREL/CP-570-30535.

40 R. A. Varin and Z. S. Wronski, in *Renewable Hydrogen Technologies, Production, Purification, Storage, Applications and Safety*, eds. L. M. Gandia, G. Arzamendi and P. M. Diéguez, Elsevier, 2013, p. 293.
41 C. M. Jensen, D. Sun and B. Lewandowski, *Proc. 2001 US DOE Hydrogen Program Review*, Baltimore, USA, 2001, p. 500.
42 M. Ichikawa and N. Kariya, *Petrotech*, 2004, **27**, 57.
43 G. Maria, A. Marin, C. Wyss, S. Muller and E. Newson, *Chem. Eng. Sci*., 1996, **51**, 2891.
44 M. Gupta, C. Hagen, W. C. Kaska, R. E. Cramer and C. M. Jensen, *J. Am. Chem. Soc*., 1997, **119**, 840.
45 C. M. Jensen and K. J. Gross, *Appl. Phys. A*, 2001, **72**, 213.
46 J. Graigm, *US Patent 6,074,447 A*, 2000 (*Chem. Abstr*., 2000, **133**, 7124).
47 A. Singaravelu, G. Balakrishnan and A. Troy, *WO Patent 2005086704 A3*, 2005 (*Chem. Abstr*., 2006, **143**, 268813).
48 M. I. Attalla, A. M. Vassallo, B. N. Tattam and J. V. Hanna, *J. Phys. Chem.*, 1993, **97**, 6329.
49 M. Matzke and J. Mittendorf, *Jpn. Patent 198469 A*, 2001 (*Chem. Abstr*., 2002, **94**, 19818).
50 G. Giacomazzi, *Erdoel & Kohle, Erdgas, Petrochemie*, 1988, **41**, 409.
51 J. Chen, F. Wu and Y. Zhu, *Taiyangneng Xuebao*, 1998, **19**, 360.
52 T. Osamu and R. Katsuniko, *Jpn. Patent 035300 A*, 2004.
53 T. Nakabayashi, *US Patent 20040026759 A1*, 2004 (*Chem. Abstr*., 2005, **140**, 173440).
54 A. Roland, M.Keller, K. Stefan, P. Heiko, K. Jens and F. Reinhard, *Jpn. Patent 083385 A*, 2004.
55 S. Nakagawa, S. Murata, M. Nomura and T. Sakai, *Bull. Chem. Soc. Jpn*., 1996, **69**, 1599.
56 S. Nakagawa, T. Ono, S. Murata, M. Nomura and T. Sakai, *Stud. Surf. Sci. Catal.*, 1996, **100**, 499.
57 E. Newson, T. B. Truong and P. Hottinger, *Proc. 12th World Hydrogen Energy Conference*, Buenos Aires, 1998, p. 935.
58 J. Chen and S. Lu, *Shiyou Daxue Xuebao, Ziran Kexueban*, 1998, **22** (5), 90.
59 R. O. Loutfy and E. M. Veksler, *Proc. International Hydrogen Energy Forum*, 2000, Munich, p. 335.
60 V. H. Agreda, L. R. Partin and W. H. Heise, *Chem. Eng. Prog*., 1990, **86**, 40.
61 S. Hodoshima, H. Arai and Y. Saito, *Int. J. Hydrogen Energy*, 2003, **28**, 197.
62 S. Hodoshima, H. Arai, S. Takaiwa and Y. Saito, *Int. J. Hydrogen Energy*, 2003, **28**, 1255.
63 S. Hodoshima and Y. Saito, *J. Chem. Eng. Jpn*., 2004, **37**, 391.
64 S. Takaiwa, S. Hodoshima, H. Arai and Y. Saito, *Suiso Enerugi Shisutemu*, 2001, **26** (2), 44.
65 S. Hodoshima and Y. Saito, *Suiso Enerugi Shisutemu*, 2000, **25** (2), 36.
66 C. Shinohara, S. Kawakami, T. Moriga, H. Hayashi, S. Hodoshima, Y. Saito and S. Sugiyama, *Appl. Catal. A*, 2004, **266**, 251.
67 Y. Saito, *Shokubai*, 2001, **43**, 259.
68 P. G. Peter and S. A. Raimond, *Eur. Patent 1475349 A2*, 2004 (*Chem. Abstr*., 2006, **141**, 368467).
69 Y. Saito, *Eco Industry*, 2002, **7** (8), 29.
70 N. Hiroshi and U. Yoshiyuki, *Jpn. Patent 056702 A*, 2000.
71 A. Neubauer and C. Ziegler, *Jpn. Patent 040601 A*, 2003.
72 W. I. F. David, M. Sommariva, P. P. Edwards, S. R. Johnson, M. O. Jones and E. A. Nickels, *US Patent 8,431,279*, 2013 (*Chem. Abstr*., 2013, **150**, 241825).
73 G. Jean, *Jpn. Patent 196638 A*, 2004.
74 K. Chen, Z. Zhang, Z. Cui and D. Yang, *Cuihua Xuebao*, 1997, **18** (2), 106.
75 C.-S. Liu, M. Sakaguchi and Y. Saito, *Suiso Enerugi Shisutemu*, 1997, **22** (1), 27.
76 A. Vaz Guy, *Jpn. Patent 212800 A*, 2003.
77 T. Akihiro and K. Hiroyuki, *Jpn. Patent 277003 A*, 2003.
78 A. L. Tarasov and L. M. Kustov, *RF Patent 2138329*, 1998 (*Chem. Abstr*., 2000, **133**, 209640).
79 C. Changpin and C. Lixin, *Chinese Patent 1380136 A*, 2002 (*Chem. Abstr*., 2003, **140**, 44242).
80 L. M. Kustov, A. L. Tarasov, V. I. Bogdan and A. L. Kustov, *RF Patent 2005130340*, 2005 (*Chem. Abstr*., 2007, **146**, 382750).
81 A. Yu. Stakheev, O. P. Tkachenko, K. V. Klement'ev, W. Grünert, G. O. Bragina, I. S. Mashkovskii and L. M. Kustov, *Kinet. Catal*., 2005, **46**, 114 (*Kinet. Katal*., 2005, **46**, 122).
82 A. L. Astakhov, A. Yu. Stakheev, N. S. Telegina and L. M. Kustov, *Book of Abstracts, EuropaCat-5*, Limerick, Ireland, 2001, vol. 5, 1-P-61.
83 L. M. Kustov and I. M. Sinev, *Russ. J. Phys. Chem. A*, 2010, **84**, 1676 (*Zh. Fiz. Khim*., 2010, **84**, 1835).

Received: 16th August 2013; Com. 13/4184