ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 4, pp. 740–751. © Pleiades Publishing, Ltd., 2007.
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Application of Clathrate Compounds for Hydrogen Storage

A. Yu. Manakov and S. S. Skiba

Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,
pr. Akad. Lavrent'eva 3, Novosibirsk, 630090 Russia
tel.: (8-383) 339-13-46
fax: (8-383 330-94-89
e-mail: manakov@che.nsk.su

Received September 27, 2006

Abstract—The review considers current works on clathrate hydrogen compounds, aimed at creating hydrogen accumulators suitable for practical application. Analysis of published data showed that clathrate hydrates formed by pure hydrogen are unsuitable for this purpose in view of their fairly low limiting hydrogen content and the necessity for their synthesis of extremely high pressures (>100 MPa) that are still industrially unfeasible. The possibilities for hydrogen storage in double (including auxiliary guest molecules along with hydrogen) clathrate hydrates are considered. It is concluded from published data that sorbents on the basis of the so-called "metal–organic frameworks" (MOFs) with a pore size of 1–2 nm hold a greater promise for hydrogen storage at temperatures of about 100 and moderately (up to 10 MPa) high pressures, but the development of all the considered methods of hydrogen storage has not yet grown out of laboratory experiments.

DOI: 10.1134/S1070363207040354

INTRODUCTION

Hydrogen is presently considered as one of promising ecologically clean energy carriers for transport of the future. Therewith, the use of a combination of a hydrogen–air fuel cell and electric engine, rather that substitution of fossil fuels in internal combustion engines (ICEs) by hydrogen is considered to hold the greatest promise [1]. A necessary condition for the realization of this strategy, especially on motor trans port, is development of small-sized high-capacity hydrogen accumulators that would provide, comparing in weight in size with contemporary petrol tanks, vehicle haulage of several hundred kilometers. The nearest performance targets of the U.S. Department of Energy (DOI) for economic on-board hydrogen accumulators for vehicles are the hydrogen capacity of no less than 6.5 wt% hydrogen per accumulator weight and the hydrogen weight density of no less than 62 kg m^{-3}. The existing and presently developed methods of hydrogen storage have been reviewed in [1–3].

Gases are most commonly stored in high-pressure cylinders (compressed gas) and lowtemperature tanks (liquefied gas). The uses of compressed natural gas and propane–butane mixture liquefied under pressure for fueling ICEs in cars and buses is well known. Even though the chemical energy contained in one atomic mass unit of hydrogen (142 MJ kg^{-1}) is almost three times higher than that in hydrocarbons (45–55 MJ kg^{-1}), to store hydrogen in cylinders at commercially mastered pressures is unprofitable because of the low molecular weight of hydrogen. Actually, methane (the principal component of natural gas) stored in a 40-l cylinder and compressed to 20 MPa will give about 350 MJ of heat on combustion, whereas hydrogen under the same conditions, as little as 87.5 MJ. This given circumstance makes us to consider vessels produced from modern composite materials with working pressures of up to 80 MPa as promising hydrogen containers. This method of storage is the most vulnerable in terms of safety because, in the case of a probable car collision, the threat of breaking of a 80-MPa gas cylinder and rather probable subsequent explosion of the air–hydrogen mixture will scarcely leave chances of survival for participants of the accident.

The boiling point of liquid hydrogen at atmospheric pressure is 21.2 K and the critical temperature is 33 K, which makes irrational and dangerous the storage of liquid hydrogen in closed vessels at increased pressures. On-board vehicle cryogenic containers for storage of liquid hydrogen, operating at atmospheric pressure, are quite feasible from the technical viewpoint. Liquid hydrogen was repeatedly used as a fuel for space crafts and planes. The most serious problem here are high energy inputs for hydrogen liquefaction and appreciable evaporation losses of hydrogen. The minimum theoretical energy demand for hydrogen liquefaction makes about 10% of the energy produced by combustion of the same quantity of hydrogen, whereas the real technological expenses reach almost 50%. Safety issues of cryogenic hydrogen storage seem, too, not be solved completely.

The above-considered methods provide effective hydrogen accumulation and are associated with extreme, for usual technics, physical parameters (gas pressures up to 100 MPa, temperatures below the liquid nitrogen temperature). Hydrogen storage under milder conditions is possible in the chemically bound state. The process should ideally be reversible, and the equilibrium thermodynamic parameters of the system are probably close to room temperature and atmospheric pressure. The physical sorption of hydrogen on carbon sorbents (including nanotubes) has been studies fairly actively. The scatter of published results is rather wide, from absolutely fantastic (and after denied) 50–60 wt% of hydrogen sorbed in nanotubes to ~1 wt% at room temperature and pressures of above 10 MPa. Most published values do not exceed 3 wt% (at 77 K), which fits well the value for a monolayer of hydrogen sorbed on one side of a graphene layer. The sorption of hydrogen on microporous carbon sorbents (including nanotubes) may result in much higher hydrogen contents. Thus, for example, calculations predict that hydrogen contents in carbon nanotubes can reach 9.6 wt% at 10 MPa and 77 K.

Certain intermetallic compounds chemically bind hydrogen in fairly mild conditions. For example, the equilibrium pressure and temperature of coexistence $LaNi_5$ and $LaNi_5H_{6.5}$ are 0.2 MPa and 25°C, respectively, and the direct and reverse reactions proceed fairly fast. The volumetric content of hydrogen in $LaNi_5H_{6.5}$ is higher than in liquid hydrogen. Other compounds have similar characteristics. Hydride hydrogen accumulators have long been applied in technics, but their wide use in vehicles is prevented by a fairly low weight fraction of hydrogen in hydrides. The above-mentioned $LaNi_5H_{6.5}$ contains no more than 1.37 wt% of hydrogen and Mg_2NiH_4, 3.59 wt%. Until now these characteristics could not be improved considerably. Now light metal hydrides (MgH_2, $LiBH_4$, $NaAlH_4$) are considered to hold greater promise in this respect, but here, too, decomposition and subsequent hydrate formation demand significant power inputs.

Summarizing the aforesaid, we can state that hydrogen accumulators for mobile applications have not yet developed. In this connection various classes of compounds are being extensively tested as hydrogen storage systems. The focus of the present review is clathrate compounds.

CLATHRATE COMPOUNDS

Clathrate compounds are formed by inclusion of molecules of one sort, called guests, into a cavity of the crystal skeleton formed by other molecules called hosts, and, therewith, the thus the guest–host interaction is purely van der Waals [4]. The often used term “inclusion compounds” is slightly broader and relates to compounds with various types of guest–host interactions in which complementarity of the guest molecule in size and shape to the host cavity affects significantly the possibility of formation and/or stability of the compound. As a rule, clathrate (inclusion) compounds are classed in terms to the host type (clathrate hydrates in which the host skeleton is formed by water molecules) [5, 6], hydroquinone clathrates [7], etc.) or in terms of discoverer’s name (Shaeffer clathrates [8]). Though zeolites and zeolite-like compounds fully meet the above criteria, they are usually not classed with clathrates in the modern literature. In this review we, too, will not touch on issues of hydrogen storage with use of zeolites. In terms of the shape of the free space in the host skeleton, cell (the space is shaped as a closed cell; clathrate hydrates are a typical example), channel (tubulates, urea clathrate), and layered (graphite inclusion compounds) clathrates are recognized. It is clear that the division into cell and channel compounds is a little bit conditional and depends on the size of the guest molecule. The most detailed description of various classes clathrates can be found in a five-volume book “Inclusion Compounds” (Atwood, J.L, Davies, J.E.D., and MacNikol, D.D., Eds., London: Academic, 1984) and recently issued ten-volume book “Comprehensive supramolecular chemistry” (Atwood, J.L, Davies, J.E.D., MacNikol, D.D., and Vogtle , F., Eds., Oxford: Elsevier, 1996), two thematic issues of the “Zhurnal Strukturnoi Khimii” (1999, vol. 40, no. 5 and 2005, vol. 46, appendix), as well as in classical works [9, 10].

In most cases, thermodynamically stable is a nonclathrate crystal modification of the host molecule, usually labeled α-H. Because of the presence of cavities in the crystal framework and, as a result, lower packing density, clathrate modifications (β-H, χ-H...) in the absence of guest are metastable with respect to α-H or absolutely unstable (labile). The formation of a clathrate compound can be presented by the following scheme: $G + n\ (\alpha\text{-H}) \rightleftarrows G \cdot n\ (\beta\text{-H})$. The β-framework here is stabilized by nonvalent guest–host interactions, and stability of the clathrate compound is, as a rule, is proportional to the energy of this interaction. A classical example of exclusively dispersion guest–host interactions is provided by the increasing in the Ar–Cr–Xe series dissociation pressures at 298 K and decomposition enthalpies (kJ mol^{-1} guest) of the hydroquinone clathrates with argon (0.34 MPa, 25.1 kJ mol^{-1}), crypton (0.04 MPa, 26.5 kJ mol^{-1}), and xenon (0.006 MPa, 32.2 kJ mol^{-1}) [4]. Dipole–dipole and dipole–induced dipole interactions favor higher stability of the compounds. Thus, the respective parameters for the hydroquinone clathrate with HCl (isoelectronic to argon, and, correspondingly, have a close energy of dispersion interactions) are 0.001 MPa and 38.5 kJ mol^{-1}. The low energy of dispersion interactions and nonpolarity entail a low clathrate-forming ability of hydrogen, associated with fact that the β-framework here is impossible to stabilize by guest–host interactions. Perhaps the only known example of a clathrate compound with a labile host framework and hydrogen as a guest are hydrogen clathrate hydrates produced at high pressures. The use of such clathrates for hydrogen storage will be discussed below.

In the case of a β-framework metastable with respect to the nonclathrate modification, a possibility exists of obtaining a compound with a clathrate structure but without guest molecules filling framework cavities and thus showing a zeolite-like behavior. From the practical viewpoint of particular interest are compounds with a channel-shaped free space, as they can act as microporous (sometimes, mesoporous) sorbents for a great variety of compounds, including hydrogen. It will be recalled that microporous are sorbents with the particle size less than 2 nm and mesoporous are those with the particle size 2–50 nm. Besides zeolites, a long-known clathrate compound of this type is the polymorphic modification of the complex [Ni(4-methylpyridine)$_4$(NCS)$_2$], so-called β-[Ni(4-methylpyridine)$_4$(NCS)$_2$] phase [8]. This compound was used to develop sorption procedures for separation of the *ortho*, *meta*, and *para* isomers of benzene derivatives, and it was also used as a stationary phase in chromatography. Until recently only few examples of such compounds have been known but now the situation is rapidly changing. Special interest is presently given to compounds on the basis of the so-called metal–organic frameworks (MOF structures), many of which are capable of reversibly sorbing gases, including hydrogen, The information on hydrogen storage in such frameworks is considered in Isaeva's review in this issue.

HYDROGEN STORAGE IN CLATHRATE HYDRATES

Clathrate hydrates are inclusion compounds whose crystal lattice is formed by hydrogen-bonded water molecules. Guest molecules reside in polyhedral cavities of the lattice. Guest–host interactions in clathrate hydrates are, as a rule, purely van der Waals. Clatrates with gaseous guests (C^1–C^4 hydrocarbons, noble gases, freons, etc.) are called gas hydrates. The overwhelming majority of gas hydrates formed at pressures close to atmospheric relate one of the three structural types: cubic structure I (CS-I), cubic structure II (CS-II), and hexagonal structure III (CS-III, "structure H" in the English-language literature). These structures can be presented as packing of water polyhedra with tops formed by oxygen atoms, edges formed by hydrogen bonds, and edgeshared adjacent polyhedra. The most common polyhedra are pentagondodecahedra (labeled 512, i.e. polyhedra with 12 pentagonal cavities, *D* cavities), *D*' cavities (435 663), 14-hedrons or *T* cavities (51 262), 16-hedrons or *H* cavities (51 264), and 20-hedrons or *E* cavities (51 268). The available information on gas and clathrate hydrates is considered in [6, 11–14], and selected structural information on hydrates is presented in Table 1.

Hydrogen hydrates have probably been first reported by Namiot and Bukhgalter [15], who discovered solid solutions on hydrogen in ice Ih. The research on hydrogen hydrates at ultrahigh pressures, undertaken by Vas et al. [16], was stimulated by the interest in the structure and composition major planets of the Solar System, whose atmospheres (and, most likely, solid nuclei) contain both water and hydrogen. Finally, hydrate formation in the water–hydrogen system in the pressure range 50–700 MPa, studied by Dyadin et al. [17], gave a general idea of hydrate formation in this system.

The presently available experimental data for the phase diagram of the water–hydrogen system are presented in Fig. 1. In the given section we use the following symbols: g for the gas (fluid) phase; l_1 for the water-rich liquid phase; i_Ih, i_{II}, i_{Ic} for ices Ih, II, and Ic; α, β, γ for solid solutions on the basis of ices Ih, II, and Ic, respectively; and h_i for gas hydrates on the basis of polyhedral frameworks. The initial portion of the $l_1$ag curve corresponds to the decomposition of solid solutions of hydrogen in ice Ih [17, 18], which shows up in a slight increase of the decomposition point of the solid solution in comparison with the ice melting curve. According to [15], at temperatures close to 0°C and 30 MPa, the solubility of hydrogen in ice makes 64% of its solubility in liquid water

Table 1. Certain structural characteristics of gaseous hydrates and ices

Structure type	Unit cell formula	Symmetry, unit cell parameters	Free diameters of cavities and channels
CS-I	$6T \cdot 2D \cdot 46H_2O$	$Pm3n$, a = 12 Å	T 5.3; 6.4 Å, D 5.2 Å
CS-II	$8H \cdot 16D \cdot 136H_2O$	$Fd3m$, a = 17.1 Å	H 6.6 Å, D 5.2 Å
HS-III	$E \cdot 2D' \cdot 3D \cdot 34H_2O$	$P6/mmm$, a = 12.3 Å, c = 10.2 Å	E 7.3; 9.6 Å, D, D' about 5 Å
Ice Ih	$2G \cdot 4H_2O$	$P6_3/mmc$, a = 4.48 Å, c = 7.31 Å	Three-dimensional system of channels, d_{max} = 2.94 Å
Ice Ic	$8G \cdot 8H_2O$	$Fd3m$, a = 6.35 Å	Three-dimensional system of channels, d_{max} = 2.88 Å
Ice II	$6G \cdot 36H_2O$	R-3, a = 12.98 Å, c = 6.25 Å (in hexagonal packing)	Channels along the c axis, d_{max} = 3.16 Å

under similar conditions. Daydin et al. [17] have analyzed the phase diagram to conclude that the water–hydrogen system at 100–360 MPa contains a hydrate with a classical polyhedral structure, and, therewith, existence of solid solutions with multiple guest occupancies is quite probable (l_1h_1g curve). Structural research on hydrates in the hydrogen-water system provided evidence for the clathrate structure of the h_1 hydrate [19]. According to this work, the crystal framework of the host in this hydrate has structure CS-II in which small cavities are occupied by “clusters” of two water molecules and larger cavities, by “clusters” of two water molecules (h_1 phase) [19]. Lokshin et al. [20] performed a more detailed neutron diffraction study of hydrogen contents in the h1 hydrate. The referees state that the highest possible occupancy of a D cavity is one hydrogen molecule. It was shown that at a pressure of 200 MPa and temperatures below 190 K, large H and small D cavities are occupied by 4 and 1 hydrogen molecules, respectively, while at a higher temperature, the occupancy of the large cavity becomes to decrease. As shown, the hydrogen hydrate synthesized at high pressures can be hardened (i.e. it can exist some time in the metastable state at atmospheric pressure, being quenched at a temperature much lower than its decomposition point, here in liquid nitrogen); therewith, at atmospheric pressure the occupancy of large H cavities rapidly decreases with increasing temperature. Thus, at the liquid nitrogen temperature the large cavity is occupied by four H_2 molecules, whereas at 160 K, by two. Further rise in the temperature leads to decomposition of the hydrate. The occupancy of small cavities begins to decrease above 160 K. Thus, the presently available of hydrogen occupancies of small cavities is contradictory. It should be noted that double H_2 occupancies of small cavities were also reported by in [21, 22], but, according to the observations in [21], hydrogen tends to “escape” the hydrate framework even at the liquid nitrogen temperature.

The $l_1\beta g$ curve for the hydrogen–water system corresponds to the decomposition of the hydrogen hydrate with the ice II framework [16, 23]. At a pressure of about 2.3 GPa a new phase χ appears in the system, which, according to the cited works, is stable at least up to 30 GPa. The single crystal X-ray diffraction analysis of this this hydrate showed that the structure of its water framework corresponds to a slightly stretched cubic ice Ic framework whose cavities accommodate hydrogen molecules. This structure undeniably resembles the ice VII structure existing in similar heat/pressure conditions and representing two interpenetrating but independent ice Ic frameworks. In the hydrogen hydrate, H_2 molecules occupy sites corresponding to those of oxygen atoms in one of ice VII sublattices, and, therewith, hydrate formation involves a noticeably weaker stretching of hydrogen bonds (to 2.79 and 2.89 Å for hydrate and ice VII, respectively is required.

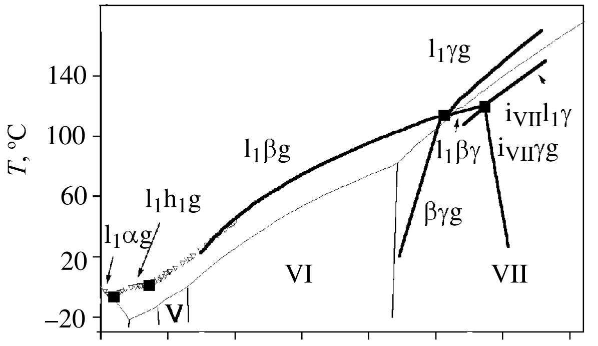

Fig. 1. Phase diagram of the hydrogen–water system [15–17]. Roman numerals denote the existence fields of the corresponding ices.

As follows from the aforesaid, of certain interest for hydrogen storage applications is polyhedral hydrate CS-II (h_1 phase) which exists in the pressure range 100–360 MPa, whereas the other hydrogen hydrate either contain very little hydrogen (α phase) or demand too high pressures to form (β and γ phases). Considering that the unit cell of structure CS-II has the formula $8H \cdot 16D \cdot 136H_2O$, i.e. it contains 8 large cavities, 16 small cavities, and 136 water molecules, it can be predicted by calculations that even under the "optimistic" assumption of the preparation of a hydrate with four hydrogen molecules in each large cavity and two hydrogen molecules in small cavities, the stoichiometry of the hydrogen hydrate will correspond to the formula $H_2 \cdot 2.125H_2O$, and the highest possible hydrogen contents of this hydrate will be 5.2 wt%. This value is noticeably lower that the targeted 6.5 wt%, and to prepare such hydrate will require pressures above 100 MPa still poorly mastered commercially. The behavior of such hydrate at low pressures and temperatures has noot been studied, but it is rather probable that it is metastable and steadily decomposes in these conditions. All this, in author's opinion, makes hydrogen hydrate CS-II an unlikely candidate for hydrogen accumulators.

There is abundant reported evidence showing that the decomposition point of hydrates formed by a mixture of hydrate-forming components are higher than those of hydrates of individual components [24]. This effect was most commonly observed with mixtures whose components strongly differing from each other in size, and it is probably explained by the formation of a hydrate in which each of type of cavities is filled by their best fitting guest molecule. As a result, a densely packed framework arises, which imparts a greater stability to the double compound [25]. There are presently attempts to make use of this effect to increase the decomposition point of hydrogen hydrate. In [26–28], hydrate formation in the THF–hydrogen–water systems was studied. Pure THF forms hydrate CS-II with large cavities fully occupied by THF molecules and vacant small cavities. Its stoichiometry is $THF \cdot 17H_2O$, the decomposition point is 4.2°C at atmospheric pressure and decreases with increasing pressure [29]. If small D cavities are filled with hydrogen molecules, the behavior of the hydrate radically changes. As with other double hydrates [30–32], the melting point of this hydrate increases with increasing pressure, but at pressures below 10 MPa the gain in the decomposition point of the double hydrate is no more than 3°C [26, 33]. The hydrogen content of this hydrate is no higher than 2.1 wt%. As shown by Lee et al. [28], when hydrate formation occurs in a THF solution with the water: THF ratio less that 17, large cavities of the CS-II framework can be occupied by hydrogen rather THF molecules. Therewith, the highest hydrogen content the referees managed to attain was 4 wt%. Rovetto et al. [33] studied a fragment of the $THF–H_2–H_2O$ phase diagram in the concentration range 2.35–11.05 mol% THF in the pressure range 2.0–13.0 MPa. The highest stability of the hydrate was observed at the THF concentration 5–6 mol%, which corresponds to a hydrate with large cavities filled with THF molecules. Besides, double hydrogen hydrates and with other organic compounds, such as a water-soluble 1,3-dioxolane and a water-insoluble 2,5-dihydrofuran, were studied [33]. They all form CS-II hydrates. The decomposition points of double hydrogen hydrates in these systems decrease in the order THF > tetrahydropyran > 2,5-dihydrofuran > 1,3-dioxolane.

Thus, the authors of the cited works have demonstrates the feasibility of preparing double clathrate hydrates having hydrogen an one of the guest components and positive decomposition points at atmospheric and slightly increased pressures. Since double hydrates of volatile organic liquids like THF are impossible to use in practice, they can be considered as no more than models. Much closer to real needs are hydrates of quaternary ammonium salts (QASs), whose melting points are close to room temperature, small cavities are vacant, and the guest is nonvolatile. The structural diversity of QAS hydrates is much broader than that of gas hydrates [6]. Unfortunately, double hydrates of hydrogen and QASs have not yet been studied. Of principal importance for practical purposes is the question whether double QAS hydrates in which most large cavities are occupied by hydrogen rather than QAS molecules are feasible. Such hydrates should have a fairly weight fraction of hydrogen, and, at the same time, QAS molecules remaining in the framework should provide a reasonable decomposition point. In authors's opinion, QAS hydrates can be used to develop a fairly efficient stationary accumulators of hydrogen and other gases, and simultaneous accumulation in the hydrates of gas and cold (QAS hydrates are considered as possible cold-preserving agents in air conditioning systems, etc. [34]) seems particularly interesting. Prospects of the development mobile hydrogen accumulators on the basis of QAS hydrates are presently impossible to predict, laboratory studies on such hydrates are necessary.

Even though the use of mixtures of hydrogen with hydrocarbons or other gases in ICEs and FCs are considered now to hold little promise, of certain technological interest is the possibility of hydrogen storage in mixture with other gases in the form of hydrates. The function of the second gas here, as well as in the above examples, is to increase the decomposition point of the hydrate. Unfortunately, the available published information is scarce. Kim and Lee [22] have studied the CO_2–H_2–H_2O hydrate with a 20 : 80 CO_2 : H_2 molar ratio to find that it has a CS-I structure with a framework completely identical to that of the CO_2 hydrate. An NMR study showed that, at the temperature 123 K and pressure 0.1 MPa, large *T* cavities are occupied by CO_2 molecules and small *D* cavities, by either CO_2 or two H_2 molecules. Zhang et al. [35] have studied the effect of methane and propane additives to hydrogen on the decomposition points of hydrates. The effect of the composition of the gas mixture on the decomposition point of the hydrate in the CH_4–H_2–THF–H_2O system at the THF concentration in the initial solution of 6 mol% has also been studied [36]. The resulting evidence suggests that the melting point of the hydrate decreases as the hydrogen content of the gas mixture increases. Thus, at 0.97 MPa, as the methane fraction in the gas mixture is increased from 5 to 100%, the hydrate melting point increases from 278.2 to 286.7 K. As the pressure increases, the difference in the melting point increases, too.

HYDROGEN STORAGE IN SORBENTS ON THE BASIS OF METAL–ORGANIC FRAMEWORKS

Inclusion compounds on the basis of metal–organic frameworks (MOFs), “coordination polymers” inclusive, have the host lattice consisting of nodes (metal ions or oxo cations, like $Zn_4O_6^+$) coordinated simultaneously to two or more nodes of linker molecules. The free space in the framework is occupied guest molecules. Notably, far not all MOFs are capable of forming inclusion compounds, because their framework may not have pores. Most likely, the first known close relative of MOFs was Berlin blue [37] whose cubic framework includes iron ions as nodes and cyanide ions as linkers. The huge structural diversity of metal cyanides has first been demonstrated by Prof. Ivamoto and his co-workers [38–40]. New structural types of cyanide systems are still discovered. Further progress of the structural chemistry of such structures has led to the creation of MOFs. A great number of new structural types of these compounds, with various nodes and linkers, have benn prepared under various conditions [41–43]. In the most topologically simple cubic frameworks, the nodal ions/clusters locate in tops of the regular cubic network and linkers form edges of the cube and link adjacent nodes (Fig. 2, some structural types of MOFs are described in Table 2). Considerable attention is presently given to MOFs with oxo cations as nodes and polycarboxylates as linkers [44–46]. One of the simplest examples of such compounds, $Zn_4O(BDC)_3$ (labeled MOF-5 or IRMOF-1) [47], has a neutral framework with $Zn_4O_6^+$ nodes and terephthalate linkers; the structure of this compound is shown in Fig. 2. Similar cubic lattices with different linkers are characteristic of compounds labeled IRMOF-6, 8, 11, 18, 20 (Table 2). Unfortunately, in the present review we are unable to give an even brief description of other structural types; readers interested in MOF structures are addressed to reviews [41–46] and original works.

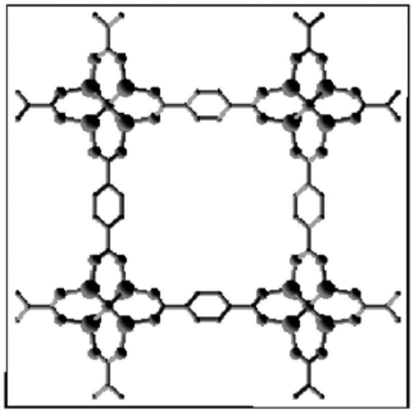

Fig. 2. Projection of the unit cell of IRMOF-1 on one of the facets.

Certain MOFs are capable to reversible guest sorption/desorption without destruction of the coordination framework, i.e. they show zeolite-like properties. The MOF framework pores suitable for accommodation of guest molecules are no larger than 2 nm, which allows MOFs to be classed with microporous sorbents. The decomposition points of MOFs do not exceed 300–500°C [44]. Unlike zeolites, MOFs are quite structurally diverse, which is associated with reach opportunities for their modification to obtain tens of compounds with the same framework topology but different nodes and linkers which can also be modified, say, by replacing methyl groups by halogens, etc. An important feature of MOFs, distinguishing them from most carbons, silicals, and other sorbents, is their ordered crystal structure, which allows these compounds to be studied by diffraction methods. Such set of properties makes MOFs a fairly perspective class of microporous sorbents. Let us consider, very briefly, some general redularities of sorption in micropores. As known [48], the sorption potential in such pores is slightly higher than on a flat surface of similar composition, because of the overlap of dispersion potentials from various pore walls. Microtimes

Table 2. Structure of certain MOFs

Denotation	MOF formula	Node	Linker	Crystal data
IRMOF-1	$Zn_4O(BDC)_3$	$Zn_4O_6^+$	benzene-1,4-dicarboxylate (terephthalate anion)	*Fm*-3*m*, *a* = 25.8320 Å[a]
IRMOF-6	$Zn_4O(BDC)_3$	$Zn_4O_6^+$	bicyclo[4.2.0]octa-1,3,5-triene-2,5-dicarboxylate	*Fm*-3*m*, *a* = 25.8421 Å[a]
IRMOF-8	$Zn_4O(NDC)_3$	$Zn_4O_6^+$	naphthalene-1,6-dicarboxylate	*Fm*-3*m*, *a* = 30.0915 Å[a]
IRMOF-11	$Zn_4O(HPDC)_3$	$Zn_4O_6^+$	4,5,9,10-tetrahydropyrane-2,7-dicarboxylate	*R*-3*m*, *a* = 24.8217, *c* = 56.734 Å[b]
IRMOF-18	$Zn_4O(TMBDC)_3$	$Zn_4O_6^+$	2,3,5,6-tetrabenzene-1,4-dicarboxylate	*Fm*-3*m*, *a* = 25.6135 Å[a]
IRMOF-20	$Zn_4O(TEC)_3$	$Zn_4O_6^+$	thieno[3,2-*b*]thiopheno-2,5-dicarboxylate	*Fm*-3*m*, *a* = 29.184 Å[a]
MOF-74	$Zn_2(DHBC)$	Zn^{2+}	2,4-dihydroxyterephthalic acid	*R*-3, *a* = 25.9322, *c* = 6.8365 Å[c]
MOF-177	$Zn_4O(BTB)_3$	$Zn_4O_6^+$	1,3,5-(4'-carboxylatophenyl)benzene	*R*-31*c*, *a* = 37.0720, *c* = 30.0333 Å[c]
MOF-505	$Cu_2(BPTC)$	Cu^{2+}	biphenyl-3,3',5,5'-tetracarboxylate	*R*-3*m*, *a* = 18.4826, *c* = 24.713 Å[d]
MIL-53(Al)	Al(OH)(BDC)	Al(OH)[a]	benzene-1,4-dicarboxylate (terephthalate anion)	*Pnma*, *a* = 17.129, *b* = 6.628, *c* = 12.182 Å[e]
MIL-53(Cr)	Cr(OH)(BDC)	Cr(OH)[a]	benzene-1,4-dicarboxylate (terephthalate anion)	*Pnma*, *a* = 17.129, *b* = 6.628, *c* = 12.182 Å[e]
HKUST-1	$Cu_3(BTB)_3(H_2O)_3$	$Cu_2(H_2O)_2$	1,3,5-(4'-carboxylatophenyl)benzene	*Fm*-3*m*, *a* = 26.343 Å[f]

[a] The nodes locate in the vertices of a regular cubic lattice and coupled together by linkers. [b] The nodes locate in the vertices of a distorted cubic lattice and coupled together by linkers. [c] Node centers locate in the nodes of a hexagonal closest packing and linked together by three. [d] The structure has two types of cavities whose packing corresponds to the packing of ions in the CsCl structure. The nodes locate along the 31(32) spiral, each linker is linked to 8 nodes to form walls of channels along the *z* axis. [e] The structure is infinite ...M(OH)M(OH)... chains held together by BDC molecules. The BDC oxygen atoms coordinate M^{3+} ions to an octahedral surrounding. [f] The nodes locate in the vertexes of a cubic lattice and linked by three.

themselves are divided into two groups: ultramicropores with sizes of no larger than 2–3 adsorbate molecular diameters and supermicropores with a larger size. Ultramicropores are filled at once, without formation of a monolayer on pore surface, whereas the fillinf process in supermicropores involves initial formation of a molecular monolayer of an adsorbate, after which the remaining narrow gaps are spontaneously filled due to overlap of the dispersion potentials of molecules entering into the adsorbate monolayers. Further increase of pore size (transition to mesopores) leads to initial mono and polymolecular adsorption on pore walls and subsequent capillary adsorbate condensation.

Of importance for sorption processes is the adsorbent–adsorbate interaction energy determining the temperature range of adsorbent performance. According to [49], the adsorbent–adsorbate interaction energy necessary for high-performance hydrogen sorption at temperatures of about 100 K is 5–6 kJ mol^{-1}, and the respective value for 300 K is no less than 15 kJ mol^{-1}. Unfortunately, experimental energies of hydrogen sorption in MOFs are scarcely available. Lona and Kaaye [50] estimated isosteric heats of sorption (Q_{st}) for hydrogen on certain ultramicroporous compounds $M_3[Co(CN)_6]_2$ (5.3–7.4 kJ mol^{-1}); for the sake of comparison, similar estimations were made for supermicroporous IRMOF-1 (about 5 kJ mol^{-1}). The greatest set of experimental Q_{st} values for hydrogen on several MOFs is presented in [51]. It is shown that the heat of sorption decreases with increasing amount of sorbed hydrogen. For example, approximation to zero adsorbate content leads to Q_{st} of 9.1 kJ mol^{-1} for IRMOF-11 and 4.9 kJ mol^{-1} for IRMOF-1. In a far-from-saturation field and at sorbed hydrogen contents of about 1 wt% for IRMOF11 and 0.8 wt% for IRMOF-1, these values are 5.1 and 4.5 kJ mol^{-1}, respectively. At higher hydrogen contents, Q_{st} decreases with increasing MOF pore size. The calculated Q_{st} for MOF-505 it is close to those for IRMOF-1 and roughly equals 6 kJ mol^{-1} [52]. The calculated energies of sorption for hydrogen on IRMOF-1 are indicative of an appreciable energy inhomogeneity of different sorption sites in the host framework, and, therewith, hydrogen is much stronger sorbed on oxo cation nodes than on organic linkers [53]. These calculation results are consistent with the experiment observation that Q_{st} rapidly decrease with increasing amount of sorbed hydrogen. It should be noted that in

Table 3. Hydrogen absorption data for certain MOFs

Denotation	Diameter min/max, Å[a]	S, $m^2 g^{-1}$ [b]	V, $cm^3 g^{-1}$ [c]	γ[d]	H_2 content, wt%		
					experiment, 77 K, 0.1 MPa	calculation by S[e]	experiment, limiting saturation at 77 K [57]
IRMOF-1	7.8/15.2	3362	1.19	0.59	1.32	6.5	5.0 (4.5 MPa)
IRMOF-6	5.9/15.2	3305	0.74	0.50	1.50	6.4	4.6 (4.5 MPa)
IRMOF-8	8.4/18.0	1466	0.52	0.66	1.50	3.0	–
IRMOF-11	6.0/12.4	1911	0.68	0.40	1.62	3.8	3.4 (3.4 MPa)
IRMOF-18	6.4/13.8	1501	0.53	0.42	0.89	3.0	–
IRMOF-20	–/17.3, –/14.0	4593	1.53	–	1.30	8.7	6.7 (7.5 MPa)
MOF-74	10.8/10.8	1072	0.48	–	1.70	2.2	2.3 (2.6 MPa)
MOF-177	9.6/11.8	4526	1.61	0.63	1.25	8.6	7.5 (7.5 MPa)
MOF-505	6.7/10.1	1646	0.63	0.37	2.48	3.3	–
MIL-53(Al)	6.4/6.4	1590	–	0.29	3.80	3.2	–
MIL-53(Cr)	6.6/6.6	1500	–	0.29	3.10	3.0	–
HKUST-1	6.9/11.1, 6.9/13.2	2257	0.66	0.41	2.50	4.5	3.1 (8.0 MPa)

[a] The minimal and maximal diameters are defined, respectively, as the diameter of a sphere capable of passing through carcass constrictions, and the diameter of a sphere that can fit in the carcass, not touching host atoms. [b] Calculated from the nitrogen absorption at 77 K by the Langmuir model. [c] Calculated from the nitrogen absorption at 77 K by the Dubinin–Radushkevich method. [d] Fraction of the empty space in the carcass by crystal data. [e] Calculated from the specific surface areas on the assumption that one hydrogen molecule occupies 0.16 nm^2 of the sorbent surface at 77 K.

terms of adsorbent–adsorbate interaction energy MOFs are quite similar to carbon sorbents, silicas, and zeolites, whose characteristic Q_{st} values are 5–9 kJ mol^{-1} [3, 51]. It is clear from these and published [49] that the accumulation in a MOF of hydrogen amounts close to limiting for the given sorbent is only possible at sufficiently low temperatures (of about 100 K).

The available literature on hydrogen sorption on MOFs are has been systematized in the recent review [54]. In what follows we will operate by data taken largely from this work. The van der Waals radius of hydrogen we take equal to 0.116 nm [55] and the adsorbent surface area occupied by a molecule of hydrogen at 77 K, to 0.16 nm^2 [56]. The density of hydrogen sorbed in micropores is taken equal to the hydrogen density at boiling point (0.7081 g cm^{-3} at 21 K). Table 3 [51, 54, 57] lists data on the weight fractions of hydrogen sorbed by MOFs at 77 K and 0.1 MPa, limiting hydrogen adsorptivities under pressure as functions of surface area S, sorbent pore volume V (both parameters were calculated from the nitrogen sorption isotherms), and the fraction of the internal MOF space available for accomodation of guest molecules (γ), calculated from crystal data. The table also lists the limiting hydrogen sorption capacities of the corresponding sorbents, calculated from the surface area S and volume V of sorbent pores. In an ideal case, for a series of sorbents from the same materials, not changing the structure depending on adsorbate amount and in the assumption of a purely physical sorption, the limiting amounts of sorbed hydrogen should be proportional S and V. Similar correlations with hydrogen sorption were repeatedly performed for carbon sorbents, zeolites, etc. [58, 59]. Moreover, until saturation has not been reached, close degrees of filling of space accessible for hydrogen should be expected for different sorbents at the same temperature and pressure.

According to data in [47], IRMOF-1 (Table 2) scarcely undergoes changes upon removal of guest molecules, and its density at removed guest is as low as 0.59 g cm^{-3}. Such an unusual property allows the limiting hydrogen sorption to be estimated by two independent methods: from nitrogen sorption (Table 3) and from the free crystal volume. The free volume in 1 cm^3 of this compound is 0.59 cm^3, which corresponds to 0.042 g of liquid hydrogen. The density of IRMOF-1 will therewith be 0.63 g cm^{-3} and the limiting hydrogen content, on the assumption of complete filling with hydrogen of sorbent micropores, 6.6 wt%. Such a simple calculation shows that in case of a rigid MOF the volume of micropores accessible for hydrogen can be reasonably estimated from nitrogen sorption data.

Table 3 shows that the weight fraction of hydrogen sorbed on MOFs 77 K and 0.1 MPa scarcely correlates with *S*, *V*, and γ even in series of compounds similar in the chemical composition and structure. Similarly, no correlation between the free volume in the framework and the weight fraction of absorbed hydrogen is observed for the series of dehydrated compounds $M_3[Co(CN)_6]_2$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) [50]. Attempted correction for the difference in the formular weight of the sorbent frameworks resulted failed to improve the situation essentially. Since significant differences in adsorbate–adsorbent interaction energies in the systems in hand seem unlikely, we can try to explain the observed anomaly by structural changes in MOF, produced by the adsorbate. Similar situations have been described in the literature [60, 61]. Under a reasonable assumption that the majority of MOFs in Table 2, unlike the above-considered IRMOF-1, noticeably change, with temperature, pressure, and even adsorbate type and content, the geometry and volume of the free space accessible for sorption, the weak correlation between the weight fraction of sorbed hydrogen and *S*, *V*, and γ becomes more understadable. Actually, in this case, the sorption of nitrogen and hydrogen can lead to deformations in MOF and significant distinctions in the free volume of the sorbent. Unfortunately, no structural evidence in favor or against this assumption is available. Additional complications are associated with fact that the surface areas and pore volumes were measured by different methods.

The hydrogen absorption isotherms at pressures of up to 0.1 MPa, reported in [61–67], revealed saturation in no one case, whereas the isotherms of nitrogen sorption on IRMOF-1 [47] and MOF-177 [68] at 78 K reach saturation at $P/P_0 < 0.2$. These data are quite consistent with the above-mentioned weak interaction of hydrogen with MOFs. The hydrogen sorption isotherms at room temperature are linear at pressures of up to 5 MPa [62, 69], i.e. the sorption in these conditions follows Henry's law. The amount of hydrogen sorbed in these conditions, as a rule, does not exceed 1 wt%; the reported 2 wt% of hydrogen sorbed at room temperature and 1 MPa cast some doubts. The low-temperature (77 K) isotherms showed a tendency for saturation [61, 64-67], but the isotherms for MIL-53 (Al) and MIL-53 (Cr) did not flatten at 1.6 MPa [61]. It should be noted that in some cases (MIL-53 (Al), MIL-53 (Cr), Table 3) the sorption isotherms showed no saturation but the weight fraction of hydrogen in sorbents at a maximum pressure was higher than the calculated limiting value. Whether it is connected with incorrect methods of the determination of surface area and pore volume or with any structural transformations in the host framework, increasing the sorption capacity, is unclear. Extremely interesting precision data on the limiting sorption of hydrogen on IRMOF-1 at 3.5 K have been reported by Yildirim and Hartman [53]. Using neutron diffraction, the referees could trace the order of filling with adsorbate molecules of various sorption sites in an MOF and also reveal an ordered arrangement of "frozen" hydrogen molecules in MOF cavities, providing accomodation in the framework of up to 10 wt% of hydrogen.

Of particular interest is the only work [57] in which hydrogen sorption isotherms were measures on MOFs at 77 K and pressures of up to 9 MPa. Selected results of this work are given in Table 3. The isotherms reach saturation at pressures of above 2 MPa (Fig. 3), and, therewith, the limiting amount of sorbed hydrogen turns to be proportional to the specific surface area of the sorbent, calculated by the Langmuir model from the adsorption of nitrogen at 77 K (Fig. 4). In the saturation region, the behavior of these systems corresponds to expectations for a purely physical sorption. It can be noted that the sorption capacities of MOFs, calculated form nitrogen sorption data, are largely overestimated with respect to experiment [57]. The most important result of the latter work is the achievement of MOF-177 and IRMOF-20 hydrogen contents of 6.5 wt%, which makes this class of sorbents suitable for mobile hydrogen accumulators. Unfortunately, the target volumetric capacity of sorbents has not yet been attained, the maximum attained value is 34 g H_2 l^{-1} sorbent for IRMOF-20, which corresponds to a 1-l cylinder with a hydrogen pressure of about 38 MPa, but the real efficiency of the accumulator will be slightly lower because of the loose sorbent packing. It should be noted that this class of sorbents gives better opportunities for optimizing sorption characteristics. It is well known that microporous sorbents generally have lower limiting capacities than macroporous but stronger bind adsorbates. The data in Table 3 clearly show that ultramiropores (smaller than 0.7 nm) and their commensurate supermicropores are filled to a greater degree than 0.11–0.18-nm pores (for 77 K and 0.1 MPa). At the same time, with too large pores (mesopores), the limiting capacity of the sorbent is lower because of the smaller surface area and impossibility of capillary condensation for a supercritical fluid like hydrogen. As the limiting sorption capacity of MOFs increases rapidly with increasing pore size and reaches practically applicable values in the case of IRMOF-20 and MOF-177, of considerable interest is further research into the regularities of hydrogen sorption in MOF supermicropores more than 1 nm in size. It can be

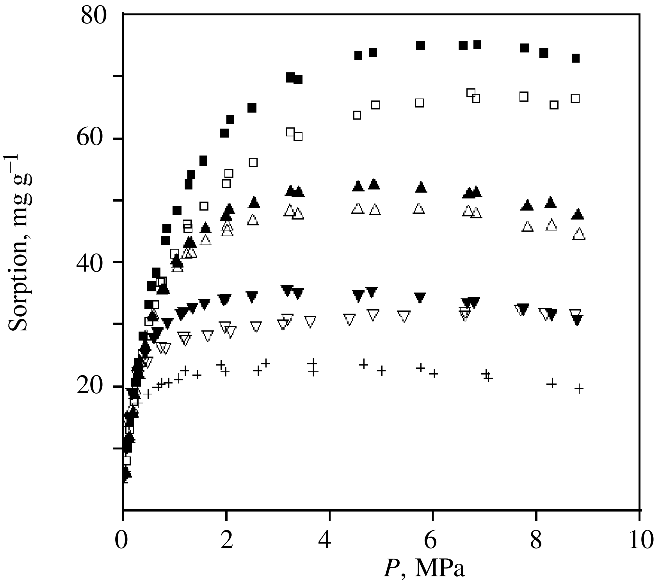

Fig. 3. Hydrogen absorption isotherms in various MOFs at 77 K and pressures of up to 10 MPa [57]:

(■) MOF-177,(□) IRMOF-20,(▲) IRMOF-1,
(Δ) IRMOF-6,(▼) IRMOF-II, (∇) HKUST-I, and (+) MOF-74.

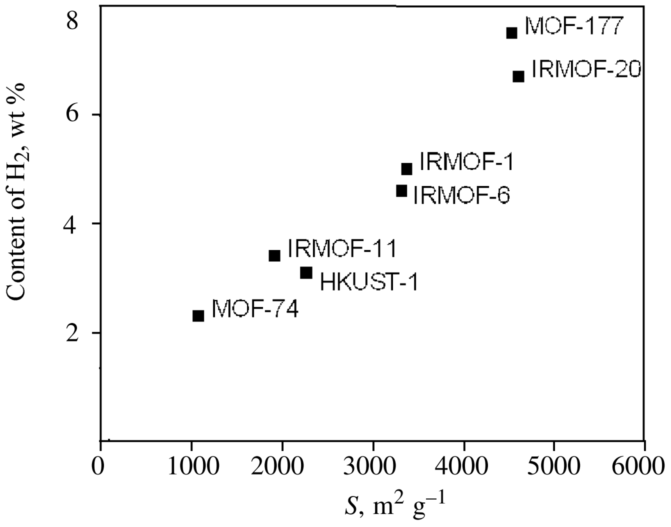

Fig. 4. Plot of the limiting quantity of sorbed hydrogen against MOF specific surface area.

expected that this research will result in the development of sorbents with record characteristics.

Summing up the aforesaid, we can state that MOFs with pores sizes of 1–2 nm are good candidates for hydrogen storage at temperatures close to 77 K and moderately high pressures. The relatively low cost of the components necessary for their synthesis, such as zinc nitrate and terephthalic acid for IRMOF-1, is no less important.

CONCLUSION

In the present review we have considered the possibility of creation of hydrogen accumulators on the basis of clathrate hydrates and metal–organic frameworks (MOFs), suitable for mobile applications. Analysis of published data showed hydrogen clathrate hydrates formed by pure hydrogen are bad candidates, which is largely associated with the fact that their synthesis demands commercially unmastered extremely high pressures (>100 MPa). Hydrogen storage in double clathrate hydrates including, along with hydrogen, auxiliary guest molecules hold a slightly greater promise. Such compounds are much more stable than pure hydrogen hydrates, and the auxiliary component can be a water-soluble nonvolatile hydrate-forming compound (such as quaternary ammonium salts) or a component of gaseous fuel (methane, propane).

It can concluded from published data that sorbents on the basis of MOFs with pore sizes of 1-2 nm are fairly promising for hydrogen storage at temperatures of about 100 K and moderately high pressures (up to 10 MPa). At present the development of all the reviewed methods of hydrogen storage techniques has not yet grown out of laboratory experiments.

ACKNOWLEDGMENTS

The authors are grateful for partial financial support to the Integration Project of SB RAS (no. 43).

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Andrei Yur’evich Manakov, Cand. Sci. (Chem.) Head of Laboratory of Clathrate Compounds, Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences. Scientific areas of focus: gas hydrates, inclusion compounds, high pressures.

Sergei Sergeevich Skiba, Post-Graduate Student, Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences. Scientific areas of focus: gas hydrates, high pressures.