INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 43 (2018) 6899–6903

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Experimental investigation of thermal insulating aerogel composites of hydrothermal reactor for biomass-to-hydrogen conversion☆

A.D. Vedenin [a,*], P.A. Vityaz [b], I.S. Ivanova [c], Yu.A. Mazalov [a], A.P. Pustovgar [c], L.V. Sudnik [d]

[a] GOSNITI, 1st Institutskiy Passage, Moscow, 109428, Russia
[b] National Academy of Sciences of Belarus, 66, Independence Ave., Minsk, 220072, Belarus
[c] Scientific Research Institute of Building Materials and Technologies, Moscow State University of Civil Engineering, 26 Yaroslavl Highway, Moscow, 129337, Russia
[d] Scientific Research Institute of the Pulse Processes of Powder Metallurgy Institute of National Academy of Sciences, 41, St. Platonov, Minsk, 220005, Belarus

ARTICLE INFO

Article history:
Received 17 January 2016
Accepted 3 November 2016

Keywords:
Hydrothermal reactor
Biomass-to-hydrogen conversion
Vacuumized thermal insulation
Hydrothermal processes
Hydrogen
Aerogel composites
SiO_2–TiO_2 composites
Heat conductivity
Hydrogen power

ABSTRACT

The paper presents aerogel SiO_2–TiO_2 composites used for thermal insulation of hydrothermal reactor for biomass-to-hydrogen conversion and the method of their production. The technology of aerogel composites production includes the following stages: ion exchange of liquid Na-glass resulting in production of silica hydrosol; hydrosol concentration; hydrogel production and its maturing; SiO_2–TiO_2 alcogel production; modification of its surface; subcritical drying of alcogel resulting in production of SiO_2–TiO_2 ambigel; its thermal treatment, granulating and classification. The influences of infrared opacifier (titanium dioxide) and thermal treatment temperature of SiO_2–TiO_2 composite on its structural and thermal characteristics have been investigated. Possibilities of hydrogen yield increase by reduction of power waste by means of vacuumized thermal insulation for reactor walls have been examined.

Introduction

Aerogels are unique form of nanoporous materials including nano-silica, which global gross output amounts to around one third of global nanoproducts production [1]. Silica aerogel is a material that is 99.8% air; that makes it the lightest solid inorganic material – it is 1000 times lighter than glass, and only four times heavier than air. Primary particles, 2–5 μm in size, are bounded in rigid agglomerated framework with mean

☆ This paper is the English version of the paper reviewed and published in Russian in International Scientific Journal for Alternative Energy and Ecology "ISJAEE", issue 187, number 23, date 14.11.2015.

* Corresponding author.
E-mail address: 1117731@mail.ru (A.D. Vedenin).

http://dx.doi.org/10.1016/j.ijhydene.2016.11.025

Acronyms/Abbreviations

ambigel	aerogel dried at atmospheric pressure
emtygel	vacuumized aerogel
12X18H10T	stainless steel 12% Cr, 18% Ni, 10% Ti
Na-glass	sodium silicate, $Na_2SiO_3 \cdot H_2O$, liquid glass
n	normal
H_2	hydrogen
SiO_2	silica, silicon dioxide
TiO_2	titania, titanium dioxide
H_2+CO	synthesis gas, syngas
CO	carbon monoxide
Si–O–Si	siloxane bond
CH_3–	methyl group

pore diameter of about 50 μm. Due to this, silica aerogels heat conductivity coefficient is 0.009–0.017 W/m·K, which is less than 0.024 W/m·K of air heat conductivity coefficient. Heat conductivity update values of various thermally insulating materials have been reported by authors in paper [2] and are represented in Fig. 1.

Silica aerogel's low heat conductivity has predetermined production of highly effective thermally insulating nanocomposites on its basis, used in hydrothermal reactor, which utilizes water under supercritical conditions ($T > 374$ °C и $P > 220$ bar) as reaction medium. Hydrothermal reactor is of tubular construction with hardened steel casing, of which outer sheath is made in the form of container containing vacuum-treated thermally insulating aerogel composite. The use of vacuum-treated thermally insulating aerogel composites for reactor thermal insulation allows reducing heat waste of reaction and utilizing conserved heat for its intensification and energy recovery efficiency upgrading.

Exothermicity of supercritical water oxidation is the main feature of hydrothermal process. If base mixture contains sufficient amount of organic substances (10%–20%), then its oxidation reaction proceeds with release of heat of 10–20 MJ/kg (for reference, release of heat while combustion of petrol is 40 MJ/kg). Heat, released during minimization of heat waste, obtained by use of vacuum-treated thermally insulating aerogel composites in reactor thermal insulation, is sufficient to provide autothermal condition of reaction and to generate electric energy and thermal power for external consumers [3].

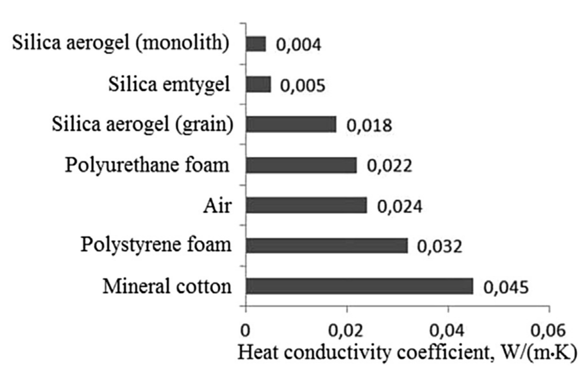

Fig. 1 – Heat conductivity of various thermally insulating materials.

Hydrothermal biomass-to-market products conversion is of physical interest along with recycling of released heat of hydrothermal processes, for instance in vapor and in gas-vapor turbine generation plants. Thus, hydrogen or H_2+CO synthesis gas could be used directly as fuel, as well as feedstock for chemical industry, food-manufacturing industry and other industries.

A major emphasis of scientists [4] investigating the influence of such parameters like temperature and reaction medium pressure, size of reactor and its constructional materials, original biomass concentration; hydrothermal process time, and use of homogeneous and heterogeneous catalysts on release of hydrogen, is placed on hydrothermal biomass-to-hydrogen conversion. This study investigates the method of vacuum-treated thermally insulating aerogel composites production and their usage effect in thermal insulation of hydrothermal reactor for biomass-to-hydrogen conversion.

Method of aerogel composites production

Development of new methods of silica aerogel production has been carried out actively in recent years [5–7]. These methods include the following basic stages as a rule: silica gel production and its maturing, and drying and thermal treatment. Drying stage is of paramount importance, as it determines the formation of silica aerogel nanoporous structure, due to which low thermal conductivity could be obtained. Although silica aerogel has been synthesized for the first time by means of drying under supercritical conditions, subcritical method of drying at temperatures up to 200 °C and at atmospheric pressure is commercially preferable [6,7]. Aerogels derived under these conditions are usually called ambigels.

Silica nanoparticles are formed at gel production stage, and then they build up rigid net structure as a result of polycondensation due to establishing of Si–O–Si siloxane bonds. It is customary to use various silanes derivatives as feedstock [5,6]. However, due to their costliness and their toxicity, as well as to nonsufficient inventory of domestic organosilicon products, method of silica aerogels production from liquid glass (sodium silicate or potassium silicate) with use of subcritical drying [7] has recently become increasingly popular.

Silica aerogel has low heat conductivity, but its radiation component is characterized by considerable increase as the temperature increases, because SiO_2 silicon dioxide absorption coefficient is very low at wavelengths below 8 μm. It is necessary to implement infrared opacifier within wavelength range of 2–8 μm in order to reduce silica aerogel heat conductivity. Carbon (soot, graphite), silicon carbide, ferrous oxides, titanium oxides, lanthanum oxides, etc. are considered to be such opacifier. TiO_2 titanium dioxide is preferable, since it is inert, commercially available and relatively inexpensive.

Method of SiO_2–TiO_2 production has included following stages: sodium metasilicate ion exchange resulting in production of silica hydrosol; hydrosol concentration; hydrogel