INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 5237–5243

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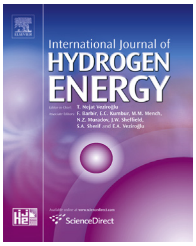

Hydrogen production through catalytic methane decomposition promoted by pure silica materials

David P. Serrano [a,b,*], Juan A. Botas [a], Patricia Pizarro [a,b], Inés Moreno [a,b], Gema Gómez [a]

[a] Chemical and Environmental Engineering Group, ESCET, Rey Juan Carlos University, C/ Tulipán S/N, 28933 Móstoles, Madrid, Spain
[b] IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935 Móstoles, Madrid, Spain

ARTICLE INFO

Article history:
Received 14 July 2014
Received in revised form
9 December 2014
Accepted 12 January 2015
Available online 12 February 2015

Keywords:
Silicas
Hydrogen
Methane
Catalytic
SBA-15

ABSTRACT

This work reports for the first time that $DeCH_4$ reaction can be carried out over pure silica porous solids working under reaction conditions similar to those employed with carbon catalysts. Thereby, a variety of pure silica samples, with different structural and textural properties have been investigated: amorphous silica (am-SiO_2), two zeolitic materials with MFI topology (conventional and hierarchical silicalite-1) and two ordered mesoporous silicas (MCM-41 and SBA-15). In all cases, the carbon generation is not observed from the beginning of the methane supply, but the presence of an induction time is noticed. This effect has been assigned to the fact that the real active sites are not present in the raw silica, being formed during the induction time by reaction between methane molecules and defective silica sites to form −Si−C− species. Among the different silica materials, great variations in the $DeCH_4$ catalytic activity are observed. The SBA-15 sample exhibits the highest activity and an exceptional stability against deactivation by carbon deposition. The major benefit derived from the use of silica materials versus ordered mesoporous carbons in $DeCH_4$ is their easier and more economical manufacture at large scale.

Introduction

The use of hydrogen as fuel provides important environmental benefits since greenhouse emissions are avoided during its combustion. This carbon footprint reduction would be reinforced if hydrogen were produced by CO_x-free routes. However, at present most hydrogen is obtained via oxidative reactions of light hydrocarbons, especially via Steam Reforming of Methane (SRM), releasing large amounts of CO_2. Moreover, the presence of CO_x disables the hydrogen so produced to be used directly in fuel cells unless it is previously purified, having a severe economic impact on its commercial viability. In this context, the most preferred technologies for hydrogen production are those using renewable raw materials and sustainable energy sources, such water electrolysis coupled with wind or solar energy. However, there are many technological and economic difficulties that must be solved prior to the commercialization of these processes [1,2].

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* *Corresponding author*. Chemical and Environmental Engineering Group, ESCET, Rey Juan Carlos University, C/ Tulipán S/N, 28933 Móstoles, Madrid, Spain. Tel.: +34 91 664 7450; fax: +34 91 488 7068.
E-mail address: david.serrano@urjc.es (D.P. Serrano).

http://dx.doi.org/10.1016/j.ijhydene.2015.01.056

In this context, decarbonization of light hydrocarbons, and in particular of methane ($DeCH_4$), is considered a clean alternative at near-term for hydrogen production until renewable energy based technologies are developed, since this process provides hydrogen and solid carbon as product, according to the following reaction [2]:

$$CH_4(g) \rightarrow C(s) + 2H_2(g)\ \Delta H^0 = 75.6\ kJ/mol \quad (1)$$

Despite having lower hydrogen yields per mol of methane molecule consumed than SRM, $DeCH_4$ is characterized by the absence of CO_x emissions and lower energy consumptions per mol of hydrogen produced (37.8 kJ/mol H_2 versus 69 kJ/mol H_2 by SRM). However, one of the main drawbacks of thermal $DeCH_4$ is the elevated temperature required, above 1200 °C, to achieve significant conversions.

Since the aforementioned benefits and limitations of thermal $DeCH_4$ were exposed, there have been numerous studies focused in the development of efficient catalysts operating at lower temperatures and providing high reaction rates [2,3]. Firstly, most efforts were paid into metal catalysts (Ni, Cu, Fe, Co, etc.) since they dramatically reduce the $DeCH_4$ threshold temperature and exhibit high reaction rates. Nevertheless, most of them are only stable at temperatures where the maximum equilibrium conversion of methane is relatively low. Moreover, taking into account the inherent difficulty for separating and recovering the catalyst from the carbonaceous deposits formed by $DeCH_4$, the cost of the metal catalysts is also an important issue. On the other hand, a second type of materials, based on carbonaceous solids, has been also extensively explored as catalysts in $DeCH_4$ reaction. Although carbonaceous catalysts require higher operation temperatures, they possess several advantages such as their higher thermal and chemical stability, as well as the possibility of working under autocatalytic conditions if they can lead to the formation of carbon deposits showing also activity for the $DeCH_4$ reaction. A large variety of commercial and synthetic carbons have been tested in $DeCH_4$ reaction, comprising very different structural and chemical properties, either from amorphous to crystalline carbons or from microporous to mesoporous carbons.

The large amount of information reported about catalytic decomposition of methane has allowed obtaining some relationships between the main catalyst properties and their activity and stability in $DeCH_4$. Thus, in the case of carbonaceous materials [4–11], those possessing a lower graphitization degree (amorphous carbons) exhibit higher catalytic activity owing to a higher proportion of defects in their structure. Concerning the resistance to deactivation by carbon deposition, textural properties play an essential role. In this way, catalysts having a high external or mesoporous surface area show a larger stability as the accessibility of the methane molecules to the active sites is kept during longer reaction times, whereas the carbon deposits may growth and/or migrate more easily towards the outer part of the catalyst particles. These facts explain the high activity and remarkable resistance to deactivation observed in ordered mesoporous carbons, in particular CMK-5, when they are used as catalysts in $DeCH_4$ reaction [12–17]. This material combines singular features as it contains a high amount of defects and possesses a bimodal system of uniform mesopores. However, CMK-type carbons are prepared by a hard-templating route, which is an expensive method and difficult to be scaled up.

In this context, the present work reports for the first time that the $DeCH_4$ reaction can be also carried out over pure silica porous solids working under reaction conditions similar to those employed with carbon catalysts. The major benefit derived from the use of silica materials versus ordered mesoporous carbons in $DeCH_4$ is their easier and more economical manufacture at large scale. Accordingly, a variety of pure silica samples have been here investigated, including amorphous silica (am-SiO_2), two zeolitic materials with MFI topology (conventional and hierarchical silicalite-1) and two ordered mesoporous silicas (MCM-41 and SBA-15). Especially remarkable are the high conversions and stability obtained over the SBA-15 material. Interestingly, SBA-15 is the hard template typically employed in the preparation of CMKs carbons.

Experimental

Synthesis of the silica samples

The silicalite-1 (silicalite-1) zeolite was synthesized by a method based on the wetness impregnation of a SiO_2 xerogel with tetrapropylammonium hydroxide (TPAOH, 40%) [18]. The silica xerogel was prepared through a two-steps sol–gel route: first, tetraethylortosilicate (TEOS, 99%) was hydrolyzed with a 0.05 M hydrochloric acid solution, using a molar H_2O/TEOS ratio = 4. Afterwards, the hydrolyzed silica precursor was condensed by drop-wise addition of 1 M NH_4OH until a gel was formed. The cogel so obtained was dried in an oven at 110 °C during 12 h. After being crushed and grinded, the solid product was impregnated with an aqueous solution of 1 M TPAOH to reach the incipient wetness point, using TPAOH/xerogel mass ratio of 1.6. The impregnated xerogel was crystallized at 170 °C under autogenous pressure during 48 h. After washing with distilled water and centrifugation several times, the silicalite-1 zeolite was calcined at 550 °C under static air.

Hierarchical silicalite-1 (h-silicalite-1) was prepared by a procedure based on the silanization of protozeolitic units previously to the hydrothermal crystallization treatment [19]. Firstly, TEOS was hydrolyzed with 1 M TPAOH aqueous solution, using a TEOS/TPAOH molar ratio of 2.23 at 0 °C. The ethanol generated during the hydrolysis step was evaporated by heating at 80 °C, the volume reduction being replaced by water addition. The gel so obtained was precrystallized at 90 °C under reflux for 23 h. Afterward, the silanization agent (phenylaminopropyltri-methoxisilane, PHAPTMS) was added in a proportion of 12% molar relative to the silica content in the synthesis media. The mixture was refluxed at 90 °C during 6 h, being subsequently crystallized by microwave heating at 170 °C for 8 h. The solid product was separated by centrifugation and washed with distilled water. After drying at 110 °C overnight, the zeolite was calcined at 550 °C under static air.

Mesostructured MCM-41 was synthesized according to the procedure reported in literature [20], using TEOS as silica precursor and tetradecyltrimethyl-ammonium bromide (TDABr) as structure directing agent. In a typical synthesis run, 2 g of surfactant were added into 475 ml of an aqueous solution containing 10% (wt) of NH_4OH, under stirring. Once