Fuel 221 (2018) 393–398

Contents lists available at ScienceDirect

Fuel

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

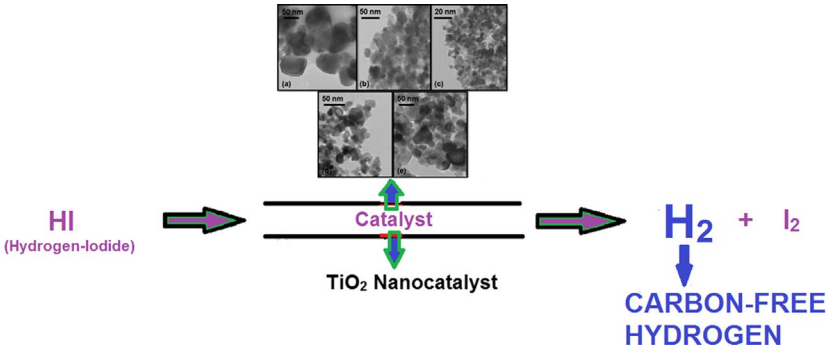
Full Length Article

TiO_2 as a catalyst for hydrogen production from hydrogen-iodide in thermo-chemical water-splitting sulfur-iodine cycle

Amit Singhania*, Ashok N. Bhaskarwar

Department of Chemical Engineering, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Titania
Catalytic activity
Hydrogen-iodide decomposition
Hydrogen
Sulfur-iodine cycle

ABSTRACT

In this work, TiO_2 nanoparticles have been prepared by the sol–gel (at different calcination temperatures) and solution-combustion method for hydrogen-iodide decomposition in thermo-chemical water-splitting sulfur-iodine (SI) cycle for hydrogen production. The sol-gel method derived TiO_2 (TiO_2-SGM-300 and TiO_2-SGM-500) provide smaller nanoparticles as compared to the solution-combustion (TiO_2-SCM). TEM revealed a particle size of around 4–5 nm of TiO_2-SGM-300. XRD and Raman confirmed that TiO_2-SGM-300 and TiO_2-SGM-500 exhibited pure anatase phase, whereas a small amount of rutile phase was observed in TiO_2-SGM-700 and TiO_2-SCM samples. It is found that with increase in calcination temperatures during sol-gel method, the average particle size of TiO_2 increases and specific surface area decreases. Commercial TiO_2 (Degussa P-25) was used for the comparison purpose. As far as the author knows, TiO_2 has been used here for the first time for hydrogen-iodide decomposition. The hydrogen-iodide decomposition experiments were carried out in a vertical-fixed bed quartz reactor at a WHSV of 12.9 h^{-1} under atmospheric pressure. The order of catalytic activity was as follows: TiO_2-SGM-300 > TiO_2-SCM > TiO_2-COMM (commercial). Also, it was observed that the hydrogen-iodide conversion decreases with increase in calcination temperatures of TiO_2 during sol–gel method. Their activity was as follows: TiO_2-SGM-300 > TiO_2-SGM-500 > TiO_2-SGM-700. TiO_2-SGM-300 catalyst also showed a reasonable time-on-stream stability of 6 h for hydrogen-iodide decomposition. The apparent activation energy of TiO_2-SGM-300 is found to be 72.29 kJ mol^{-1}. This shows that the TiO_2 has a potential of generating hydrogen from hydrogen iodide in SI cycle. This can further be explored as a catalyst support using some non-precious and precious metal catalysts for hydrogen-iodide decomposition.

* Corresponding author.
E-mail address: amit.singhania2008@gmail.com (A. Singhania).

https://doi.org/10.1016/j.fuel.2018.02.130
Received 1 November 2017; Received in revised form 16 February 2018; Accepted 20 February 2018

1. Introduction

The research on hydrogen production by different routes is increasing day by day. The continuous depletion of fossil fuels and increasing concentration of carbon dioxide raises the alarms of the world and forcing the researchers to look for alternative energy sources which must be clean, renewable and low cost [1,2]. Hydrogen is considered as a fuel of the future time. It is light, cheap, renewable and environment friendly energy carrier. It can be used in the transportation sector, home kitchen, electricity generation, electronics appliances and as a stored energy for other applications. Hydrogen can be produced by several methods such as photocatalytic water-splitting, electrolysis, thermochemical and biological methods [3–8]. But, the production of clean hydrogen on a large scale is a significant challenge. One such technology is the sulfur-iodine (SI) cycle, which is being used by researchers over the past few decades for large scale hydrogen production [9–11]. This cycle has a high efficiency of around 50% and this can be further increased by optimizing the parameters involved in the SI process [12–14]. It consists of the following reactions [15]:

Bunsen reaction:

$$SO_{2(g)} + I_{2(s)} + 2H_2O_{(l)} \leftrightarrow 2HI_{(aq)} + H_2SO_{4(aq)} (\ T= 20-120\ °C; \Delta\ H = -75 \pm 15\ kJ{\cdot}mol^{-1}) \quad (1)$$

Sulfuric-acid decomposition:

$$H_2SO_{4(g)} \leftrightarrow H_2O_{(g)} + SO_{2(g)} + 1/2O_{2(g)} (\ T= 800-900\ °C; \Delta\ H = 186 \pm 3\ kJ\ mol^{-1}) \quad (2)$$

Hydrogen-iodide decomposition:

$$2HI_{(g)} \leftrightarrow H_{2(g)} + I_{2(g)} (\ T= 400-550\ °C; \Delta\ H \sim 12\ kJ\ mol^{-1}) \quad (3)$$

Net reaction:

$$H_2O_{(l)} \rightarrow H_{2(g)} + O_{2(g)} \quad (4)$$

In Eq. (1) (Bunsen Reaction), reaction of sulfur-dioxide, iodine and water produces the mixture of hydrogen iodide and sulfuric acid. After the separation of hydrogen iodide and sulfuric acid, the two products are decomposed further in Eq. (2) (sulfuric-acid decomposition) and 3 (hydrogen-iodide decomposition). Eq. (2) generates water, sulfur-dioxide and oxygen, whereas Eq. (3) produces hydrogen and iodine. The products sulfur dioxide and water from Eq. (2) and iodine from Eq. (1) are recycled back to Bunsen reaction and this process goes on. The net sum of all the reactions involved in this cycle is the splitting of water into hydrogen and oxygen in a carbon dioxide free environment.

The decomposition of hydrogen iodide occurs very slowly, even at high temperature of 500 °C. A small amount of an active catalyst along with high thermal energy increases the rate of the reaction. It is a thermodynamic limited equilibrium reaction. In literature, various catalysts such as noble metal-based (Pt, Pd, Au, Rh, and Ir) and non-noble metal-based (Ni, Mo, Co and Ag) are reported [16–21]. O'Keefee et al. [22] showed in their review that the supported Pt catalysts gave very high activity towards hydrogen-iodide decomposition. But, Pt being a precious metal is very expensive and there is no way to think about it for future practical SI cycle.

The idea of this work is to explore the titania (TiO_2) as a catalyst for hydrogen production from hydrogen iodide in the SI cycle. TiO_2 has been chosen among different metal oxides because of interesting physicochemical and economical properties. It is abundant, inexpensive and non-toxic material which has been used in many catalytic applications such as steam reforming, oxidation of carbon monoxide, ethanol and acetaldehyde, NO_x removal, photo-catalytic water-splitting, decomposition of dyes, water-gas shift, dehydrogenation, hydro-desulfurization etc. [23–26]. TiO_2 has high mechanical resistance and good chemical and thermal stability under oxidative and acidic environmental conditions [27]. TiO_2 can act as a good catalyst if it presents at a nano scale because of numerous defects (oxygen vacancy) present on the surface at this scale. It exists in three forms: anatase, rutile and brookite. Anatase and rutile are more common forms of TiO_2. The crystalline size of rutile is always larger than the anatase phase. The anatase phase is used mainly for catalytic applications because of its high specific surface area and strong interaction with the metal nanoparticles [27]. The strong metal support interaction (SMSI) is normally seen in anatase TiO_2 and insignificant in rutile phase. The use of TiO_2 has not explored in thermo-chemical SI cycle in spite of the fact that it has been applied in various applications either as a catalyst or support. As far as the author awareness, TiO_2 is going to use for the first time in

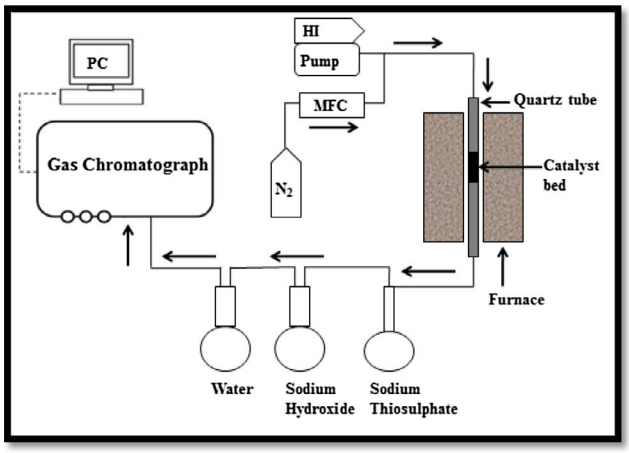


Fig. 1. Schematic diagram of testing of TiO_2 catalytic activity.

Table 1
Physico-chemical properties of synthesized catalysts.

Sample	Specific surface area ($m^2\ g^{-1}$)	Pore volume ($ml\ g^{-1}$)	FWHM (deg.)	Crystallite size[a] (nm)
TiO_2-COMM	11	0.06	0.119	71.4
TiO_2-SCM	35	0.03	0.398	21.3
TiO_2-SGM-300	101	0.15	1.587	4.2
TiO_2-SGM-500	59	0.11	0.734	11.6
TiO_2-SGM-700	14	0.05	0.223	38.1

[a] Calculated using Scherrer formula due to (1 0 1) plane.

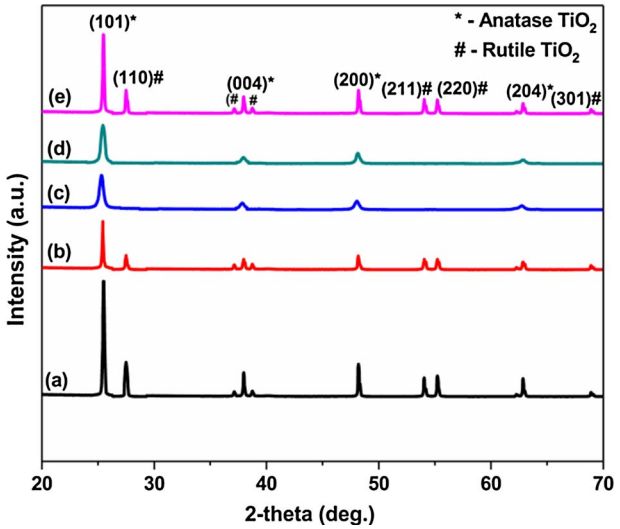


Fig. 2. Powder XRD patterns of (a) TiO_2-COMM, (b) TiO_2-SCM, (c) TiO_2-SGM-300, (d) TiO_2-SGM-500, and (e) TiO_2-SGM-700.