

# **Construction of Z-scheme Using $\text{XTiO}_3\text{:Pt}$ ( $\text{X} = \text{Ca}, \text{Sr}, \text{Ba}$ ) in Combination with $\text{WO}_3$ and $\text{BiVO}_4$ for Hydrogen Production from Water**

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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):

18th World Hydrogen Energy Conference 2010 - WHEC 2010

Parallel Sessions Book 3: Hydrogen Production Technologies - Part 2

Proceedings of the WHEC, May 16.-21. 2010, Essen

Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-3

Institute of Energy Research - Fuel Cells (IEF-3)

Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010

ISBN: 978-3-89336-653-8

# Construction of Z-scheme Using $\text{XTiO}_3\text{:Pt}$ ( $\text{X} = \text{Ca}, \text{Sr}, \text{Ba}$ ) in Combination with $\text{WO}_3$ and $\text{BiV}_5\text{O}_{14}$ for Hydrogen Production from Water

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## 1 Introduction

Modern civilization has grown greatly dependent on technology and in consequence on energy. Continuous and stable energy supplies are the basis for economic growth of every country. Most of energy used today is derived from fossil fuels. It creates many environmental problems, like acid rains or speeding up the greenhouse effect. Abundance of fossil fuels can only be found in few regions of the world. It makes other regions energetically vulnerable. Another problem is limited amount of these energy sources. In this situation, there is a great need for alternative energy sources. We need not only new energy sources but also energy carriers. Among many possible candidates, hydrogen seems like the most promising one [1].

There are many industrial methods for hydrogen production, like steam reforming of natural gas, water gas shift reaction, electrolysis of water, etc. However neither of them can be used to produce environmentally clean hydrogen because they use energy from burning of fossil fuels.

There is a great need for an efficient, clean and inexpensive method of hydrogen production. Photocatalytic splitting of water is a very promising solution. There are numerous reports of photocatalytically active transition metal oxides and sulfides capable of generating hydrogen from water [2]. Most of them absorb radiation in UV region. Ultra-violet radiation constitutes for only 4% of total radiation reaching surface of the Earth. Therefore there is a necessity for a photocatalytic system working under solar radiation. In recent years, systems based on artificial photosynthesis became studied with more interest. Many researchers attempted to create photocatalytic system based on Z scheme [3-4]. My work focuses on synthesis and characterization of perovskite based photocatalysts, modified with platinum. The perovskite structure has been chosen with regard to its versatility and ease of manipulating physical and chemical properties. This work focuses on three perovskites,  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$ . A sol-gel method has been selected for preparation of perovskites. It was expected to produce higher surface area compared to solid state reaction method. High surface area, although not directly important in photocatalysis, can provide high platinum dispersion and in consequence create many photocatalytically active sites. For oxygen generating photocatalysts  $\text{WO}_3$  and  $\text{BiVO}_4$  have been chosen.

## 2 Experimental

### Synthesis under acidic conditions

$\text{CaTiO}_3$ ,  $\text{SrTiO}_3$  i  $\text{BaTiO}_3$  were prepared by sol-gel method. As precursors  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  and  $\text{X}(\text{OOCH}_2\text{CH}_3)_2$  (where  $\text{X} = \text{Ca}, \text{Sr}, \text{Ba}$ ) were used. An exact amount of a metal acetate was dissolved in acetic acid – water solution. The ratio of acetic acid and water has been chosen to get pH value near 2. Next, the solution was added to previously prepared solution of titanium (IV) isopropoxide in isopropanol, with intense stirring. The solvents were then evaporated with continuous heating, until gel formed. The gel was aged in 70-90°C and then dried in 120°C. Prepared powders were calcined at different temperatures to give product.

### Synthesis in melted stearic acid

$\text{CaTiO}_3$  was prepared by reaction between  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_{40}$  and calcium stearate in melted stearic acid. Firstly,  $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_2\text{Ca}$  was dissolved in stearic acid melted at 80°C. Next, titanium (IV) isopropoxide was added and the solution was stirred until gel was formed. The obtained gel was left to cool down naturally. The perovskite precursor was then calcined in temperatures between 500°C to 600°C.

### Synthesis under alkaline conditions

In this method the first step was to produce gel using the same method as described in acidic synthesis paragraph. The prepared gel was then put into a stainless steel autoclave with teflon inlay. Autoclave was filled with water and pH was adjusted to 12 using KOH. Next, the autoclave was heated to 200°C for 6 hours. After that, the autoclave was allowed to cool down naturally. The prepared suspension was rinsed with methyl alcohol and water and centrifuged. Samples were dried in 120°C.

### Preparation of $\text{WO}_3$

Tungsten oxide (VI) was prepared by thermal treatment of  $\text{H}_2\text{WO}_4$  in air atmosphere.

### Preparation of bismuth vanadate

The first phase of preparation was a solid state reaction between  $\text{V}_2\text{O}_5$  and  $\text{K}_2\text{CO}_3$ , which were mixed in molar ratio 3:5. The mixture was heated to 430°C for 5 hours. The prepared  $\text{K}_3\text{V}_5\text{O}_{14}$  was suspended in  $\text{Bi}(\text{NO}_3)_3$  water solution and stirred for 72 hours. The precipitate was rinsed with water and dried at 120°C.

### Catalysts surface modification

Perovskites surface was modified with different amounts of platinum, using incipient wetness impregnation technique.

### Sample characterization

The thermogravimetric analysis was performed on Thermogravimeter Setaram Setsys 12 (TGA/DSC), in air atmosphere. A temperature from 17°C to 1000°C was used (10°C/min temperature bear). Powder X-ray diffraction was done on Bruker AXS D8 Advance diffractometer, with 20° do 70° 2θ range and using 0,02°/s measure rate.  $\text{CuK}_\alpha$  (wavelength = 1,5406 Å) was used as radiation source. Surface area was determined using full adsorption/desorption isotherm performed at Micromeritics Sorptometr ASAP 2010. The presented values of surface area were calculated with BET theory. The average pore

diameter was calculated using BJH method, based on desorption isotherm. The range of radiation absorbed by photocatalysts was measured with UV-VIS Varian Carry 100 spectrophotometer. Catalytic tests were performed in a pyrex glass reactor, illuminated with four Ultra-Vitalux lamps imitating solar radiation. The reactor was coupled with Varian CP-3800 gas chromatograph in order to measure the amount of produced hydrogen.

### 3 Results

In order to evaluate optimal calcination temperature a thermal gravimetry technique was used. The TG curves were similar to all samples synthesized under acidic conditions. A weight loss below 200°C was caused by evaporation of moisture. A massive weight loss accompanied by big exoenergetic effect in 300-400°C range can be associated with oxidation of organic compounds like acetate and isopropyl groups. Around temperatures between 600-750°C a third weight loss can be observed. It is consistent with pyrolysis of residual organic derivatives. Last weight loss, related to formation of perovskite structure, was usually observed in temperature above 800°C.

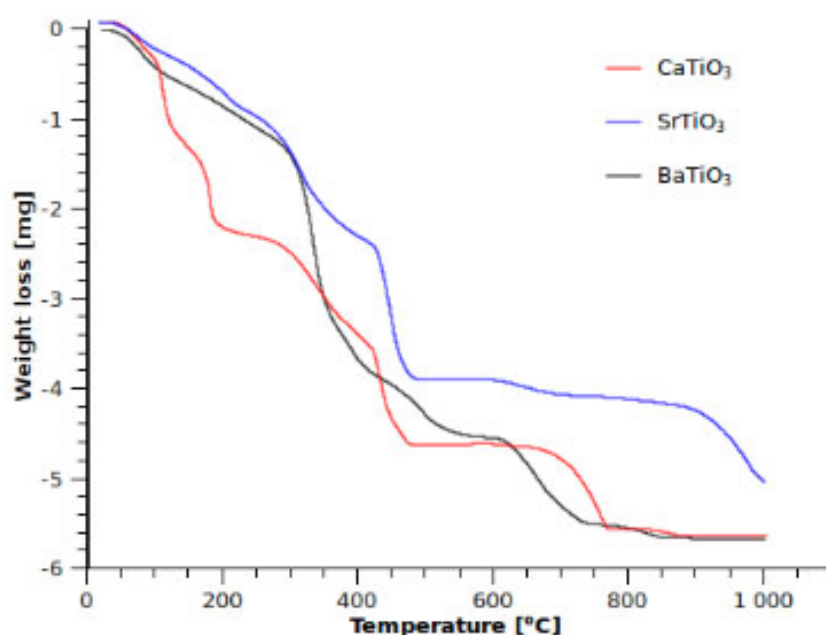
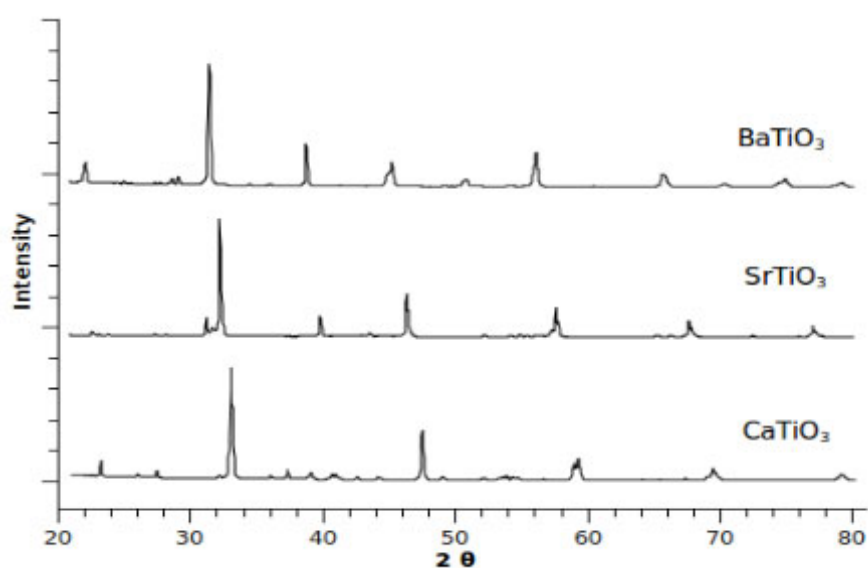


Figure 1: TG curves of CaTiO<sub>3</sub>, SrTiO<sub>3</sub> and Ba TiO<sub>3</sub> dried gels.

The XRD patterns of samples calcined at different temperatures show, that for all three perovskites the XTiO<sub>3</sub> crystalline structure is created in 800°C and higher. At low calcination temperatures additional reflexes are present, which can be associated to trace amounts of TiO<sub>2</sub> (rutile) and XCO<sub>2</sub>. At calcination temperatures above 1000°C additional phases are still visible but very weak.



**Figure 2:** XRD patterns of perovskites prepared under acidic conditions, calcined at 1000 °C.

Adsorption/desorption data shows that surface areas of samples produced by all three methods are higher compared to perovskites prepared using solid state reaction. The highest surface area was achieved for  $\text{CaTiO}_3$  prepared by synthesis in melted stearic acid - 87 m<sup>2</sup>/g.

**Table 1:** Surface areas for samples prepared under various conditions.

		Surface area [m <sup>2</sup> /g]	Average pore volume [nm]
Acidic synthesis	$\text{CaTiO}_3$ 900°C	12,2	9,5
	$\text{SrTiO}_3$ 900°C	4,5	13,7
	$\text{BaTiO}_3$ 900°C	7,9	13,9
Stearic acid	$\text{CaTiO}_3$ 500°C	87,6	15,9
	$\text{CaTiO}_3$ 600°C	42,8	16,8
$\text{BaTiO}_3$ AUTOCLAVE		23,1	7,7

In general, surface area decreases rapidly with increasing calcination temperature. Table 1 presents a comparison of surface areas of perovskites synthesized by all three methods.

Table 2 shows selected results of catalytic tests. All results are presented in μmol/h and calculated for 1 g of photocatalyst.

**Table 2: Hydrogen production after 1 h of reaction using 1 g of catalyst.**

		Calcination temperature [°C]	Amount of Pt [% wt.]	Hydrogen produced [ $\mu\text{mol/h}$ ]
$\text{CaTiO}_3$	Prepared under acidic conditions	900	0,1	46,5
$\text{CaTiO}_3$		900	0,05	64,2
$\text{SrTiO}_3$		1000	0,1	62,5
$\text{BaTiO}_3$		800	0,1	46,9
$\text{BaTiO}_3$		800	0,05	40,6
$\text{CaTiO}_3$	Prepared in melted stearic acid	600	0,1	110,7
$\text{CaTiO}_3$		500	0,1	253,1

#### 4 Conclusions

All prepared photocatalysts have higher surface areas than perovskites produced by traditional method. High loss of surface area with increasing calcination suggests need for optimizing the gelation process to make calcination at lower temperatures possible.  $\text{CaTiO}_3$  produced by synthesis in melted stearic acid is most active of all photocatalysts. The absorption band of all photocatalysts starts at approximately 400 nm which should make catalysis under Solar radiation possible.

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