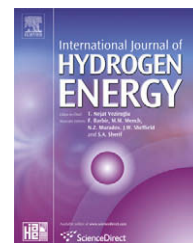


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# Decomposition of hydrogen iodide in the S–I thermochemical cycle over Ni catalyst systems

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## ABSTRACT

The sulphur–iodine thermochemical cycle for hydrogen production has been investigated by ENEA (Agency of New Technologies, Energy and Environment, Italy) over the last 5 years, with a particular focus on chemical aspects. Regarding the hydrogen iodide decomposition, four  $\gamma$ -alumina-supported nickel catalysts were produced and characterized, and then tested in terms of catalytic activity and stability by means of a tubular quartz reactor. In particular, the relationship between catalytic activity and preparation procedure was investigated. From the experimental data acquired, it can be concluded that three of the four catalysts tested demonstrated high catalytic activity, since hydrogen iodide conversion was almost coincident with the theoretical equilibrium value. On the other hand, for all the catalysts, a gradual but considerable deactivation phenomenon was observed at 500 °C, while at a temperature higher than 650 °C the catalytic activity was recovered.

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## 1. Introduction

The sulphur–iodine thermochemical cycle is one of the most promising routes currently under development for sustainable hydrogen production from water. Over the last 5 years, ENEA has been involved in a research program within the framework of the TEPSI project (TEcnologie e Processi innovativi per il Sistema Idrogeno, Innovative Technologies and Processes for the Hydrogen System) that focuses on the chemical aspects of this cycle.

The S–I thermochemical cycle is based on three main reactions carried out at three different temperature levels.

Bunsen reaction (exothermic at 20–120 °C):



Hydriodic acid decomposition (endothermic, at 300–450 °C):



Sulphuric acid decomposition (endothermic, at 800–900 °C):



Among these reactions, hydrogen iodide (HI) decomposition presents a rather low equilibrium conversion even at high operating temperatures (the equilibrium conversion at 750 K is about 0.22) and consequently a considerable energy expense for the separation and recirculation of the unreacted species is required [1]. In addition reaction (1) is carried out in water media with a relative iodine excess (eight times higher than

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the stoichiometric value) in order to induce immiscibility between the two acid solution products, i.e., sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and hydriodic acid (HI) aqueous solutions [2]. Hence, a large amount of energy is required for concentrating the two acid solutions and for removing iodine from the heavier phase containing  $\text{H}_2\text{O}$ – $\text{HI}$ – $\text{I}_2$  before HI decomposition.

For this reason, different flowsheets have been proposed in the literature with the purpose of optimizing the energy consumption related to the HI decomposition section. One of the most promising schemes is based on the use of a reactive distillation column [3,4] in which the  $\text{I}_2$  removal and HI decomposition simultaneously take place: along the column the L–V equilibrium between  $\text{HI}$ – $\text{I}_2$  and  $\text{H}_2\text{O}$  leads to the distillation of HI at the top, where the presence of a catalyst allows the HI decomposition into  $\text{H}_2$  and  $\text{I}_2$ , and the separation of liquid  $\text{I}_2$  from the bottom. This column configuration acts to shift the thermodynamically limited gaseous HI decomposition, which in addition occurs at a very low rate [5,6], toward the products ( $\text{H}_2$  and  $\text{I}_2$ ) by means of continuous  $\text{I}_2$  removal by reflux flow. The applicability of this optimized process solution strictly depends on the catalyst performance and durability in presence of the complex chemical system containing HI,  $\text{H}_2\text{O}$  and  $\text{I}_2$ . More generally, referring to all the process solutions involving the gaseous HI decomposition reaction ( $\text{H}_3\text{PO}_4$  based scheme [7], electro dialysis scheme [8]), the use of a good catalyst allows the decomposition temperature to be reduced, with the benefit of attenuation of the corrosion problems in the presence of hydrogen iodide–iodine mixtures, and enhances decomposition kinetics, with the consequent advantage of reactor size reduction. Thus, the investigation and the optimization of a proper HI decomposition catalytic system are of strategic relevance for the development of the whole S–I cycle.

The heterogeneous catalytic reaction was extensively investigated by NCLI (National Chemical Laboratory for Industry, Japan) and GA (General Atomics, USA) [9]. Different catalytic systems were found effective, in particular the Pt-supported catalysts showed very good performance with respect to activation energy values and lifetime [10–12]. Some authors proposed less costly catalysts: the cost savings resulting from the use of non-precious metals may be an advantage in the design of a plant of large size. O’Keefe et al. [9] reported that nickel was for the most part a poor catalyst, although its particular deposition on an active carbon surface produced a catalyst that was notably good. Nickel alumina-supported catalysts were also tested and demonstrated

a remarkable catalytic activity. However, operating times were limited to the 100-h range.

The aim of the present work is the analysis of the catalytic activity of four  $\gamma$ -alumina-supported nickel catalysts obtained from different preparation methods, in particular focusing on the relationship between catalytic activity and preparation procedure. Three of them were prepared from  $\gamma$ -alumina by an impregnation–calcination method and were obtained from the deposition of two different precursors, such as nickel acetylacetonate and nickel nitrate [13]. The fourth one is a nickel aluminate catalyst obtained by a co-precipitation method, prepared in order to better understand the metal–support interactions in nickel acetylacetonate catalyst and, at the same time, to test the effectiveness of this catalyst in HI decomposition.

## 2. Materials and methods

### 2.1. Catalyst preparation

Four different  $\gamma$ -alumina-supported nickel catalysts with nickel content ranging from 0.83% to 14.55% were prepared by impregnation–calcination and co-precipitation methods.

For catalysts obtained by the impregnation technique, designated Ni-acac, Ni-nitrate and Ni-nitrate15, neutral activated alumina was used (powdered  $\gamma$ -alumina of high purity from Aldrich, with the following declared physical properties: BET = 153.37  $\text{m}^2/\text{g}$ , micropore volume = 12.80  $\text{mm}^3/\text{g}$ , average particle size = 150 mesh, pH = 7.0, density = 3.97  $\text{g}/\text{cm}^3$ , melting point = 2040  $^\circ\text{C}$ ).

The Ni-nitrate catalyst was prepared by conventional wetness impregnation adopting nickel nitrate salt ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) as precursor. In particular, the alumina powder was impregnated with the nickel nitrate aqueous solution, stirred at room temperature for 5 h, filtered by membrane, and finally washed with water. The resulting solid was dried at 60  $^\circ\text{C}$  for 12 h in a  $\text{N}_2$  atmosphere, calcined in air at 550  $^\circ\text{C}$  for 10 h (under a 5  $^\circ\text{C}/\text{min}$  ramp followed by holding isothermally for 2 h), and then reduced in the presence of a gaseous mixture of  $\text{H}_2/\text{N}_2$  (1:1) at 550  $^\circ\text{C}$  (heating rate of 5  $^\circ\text{C}/\text{min}$  and isotherm of 2 h). For the Ni-nitrate15 catalyst, the impregnation was carried out adopting the same protocol, but the final washing step was avoided. The solid obtained was dried at 110  $^\circ\text{C}$  for 12 h in air, calcined in air at 450  $^\circ\text{C}$  for 4 h

**Table 1 – Physicochemical properties and preparation methods of catalysts tested.**

Catalyst	Precursor	Deposition method	Calcination conditions	Reduction conditions	Ni loading (%)	Crystal phases
Ni-acac	$\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$	Impregnation over $\gamma$ - $\text{Al}_2\text{O}_3$ (solvent: acetone)	Not executed	$\text{H}_2/\text{N}_2$ (1:1), 2 h at 500 $^\circ\text{C}$	11.93	NiO, $\text{NiAl}_2\text{O}_4$ , Ni
Ni-aluminate	$\text{Ni}(\text{OH})_2$	Co-precipitation with $\text{Al}(\text{OH})_3$ (ammonia solution)	Air, 5 h at 900 $^\circ\text{C}$	Not executed	Not available	NiO, $\text{NiAl}_2\text{O}_4$ , $\gamma$ - $\text{Al}_2\text{O}_3$
Ni-nitrate15	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Impregnation over $\gamma$ - $\text{Al}_2\text{O}_3$ (solvent: water)	Air, 4 h at 450 $^\circ\text{C}$	$\text{H}_2$ , 3 h at 500 $^\circ\text{C}$	14.55	Ni, NiO
Ni-nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Impregnation over $\gamma$ - $\text{Al}_2\text{O}_3$ (solvent: water)	Air, 10 h at 500 $^\circ\text{C}$	$\text{H}_2/\text{N}_2$ (1:1), 2 h at 550 $^\circ\text{C}$	0.83	Not available

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