

Ni catalyst deactivation in the reaction of hydrogen iodide

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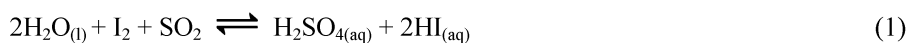
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In a previous work, it has been studied some Ni-catalysts prepared from different precursors ($Ni(C_5H_7O_2)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$) via impregnation-calcination or co-precipitation techniques, using commercial γ -alumina as support. The study pointed out a high initial conversion value for the reaction of hydrogen iodide decomposition at 500°C, but in few hours a progressive deactivation of the catalysts occurred. In order to understand this phenomena, three new catalysts have been prepared starting from $Ni(acac)_2$, using mesoporous aluminas as support. The initial conversion of HI decomposition with these new catalysts (showing a larger surface area and Ni^0 crystallites on it) was almost coincident with theoretical equilibrium value. Their deactivation at 500°C was slower than that of the catalysts studied in the previous work.

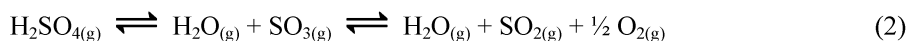
1. Introduction

H₂ production is nowadays becoming an attractive object of research in order to find an alternative energy source to conventional fossil ones, for the explosion of their worldwide costs and for the consequent geopolitical aspects. The reduction of the dependence from fossil raw materials and hence in the emissions of harmful substances in the atmosphere could be achieved only finding a way to produce H₂ starting from materials, like H₂O, which is clean, renewable and low-cost. In this directions, a lot of thermochemical water splitting cycles have been studied [2,3], which purpose is to decompose H₂O through a cycle of reactions at a temperature lower than the one required for the direct single-step decomposition. Among thermochemical processes, the iodine-sulfur (IS) process, developed by General Atomic in 70's [4,5], seems to be the most promising one [6, 7, 8]. In the last 5 years some research groups, drove by ENEA (Ente Nazionale Energie Alternative), have been involved in the TEPSI project (TEcnologie e Processi innovativi per il Sistema Idrogeno), focusing on the chemical aspects of this cycle. In particular, the aim of the research is to use solar energy for the reactions, after concentrating the sun radiations through a parabolic mirror and storing that energy using molten salts [9, 10]. The IS cycle consists of the following reactions:

1) Bunsen reaction ($T = 20^\circ\text{-}120^\circ\text{C}$; $\Delta H = -75 \pm 15 \text{ kJ mol}^{-1}$)



2) H₂SO₄ decomposition ($T = 600\text{-}900^\circ\text{C}$; $\Delta H = 186 \pm 3 \text{ kJ mol}^{-1}$)



3) HI decomposition ($T = 300\text{-}500^\circ\text{C}$; $\Delta H \sim 12 \text{ kJ mol}^{-1}$)



The 3rd reaction is slightly endothermic and requires an energy expense for the separation and recirculation of the unreacted species [12]. In order to get a higher reaction rate, a catalytic system has been used. The heterogeneous catalytic reaction was investigated by National Chemical Laboratory for Industry of Japan and General Atomic [13]. In the previous work [1], 4 different Ni-catalysts supported on commercial $\gamma\text{-Al}_2\text{O}_3$ have been tested: they gave good initial conversion value at 500°C , close to thermodynamic value. The catalysts efficiency showed a decrease after few hours of experimentation. Three new Ni-catalysts has been prepared using $\text{Ni}(\text{acac})_2$ and non-commercial mesoporous aluminas. The aim of this work is to better analyze the Ni-supported catalysts (their properties and activity) and to understand if they may be used for HI decomposition.

2. Experiment

2.1 Mesoporous alumina synthesis and characterization

The alumina *ALMN2* has been prepared dissolving Brij[®]56 surfactant ($\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_n\text{OH}$) in $\text{H}_2\text{SO}_{4(\text{aq})}$ for 3 hours at 70°C and then adding aluminum sec-butoxide (Fluka). After 1 hour of stirring, the mixture has been transferred into a Teflon-lined autoclave and microwave treated at 80°C for 30 min. Microwave heating has been carried out in a Milestone Ethos 1600 MW oven, operating at a constant output power of 300 W. After cooling, the product has been filtered, washed with EtOH for 36 hours and dried at 40°C . The alumina has been calcinated at 500°C for 1 hour ($6^\circ\text{C}/\text{min}$). The sample *ALM7N2* has been prepared in the same way, using a smaller amount of Brij[®]56 (2/3 of the previous case) and without any stirring action during the MW treatment. The surfactant has been removed by a thermal decomposition in a controlled atmosphere: 1 hour at 400°C in N_2 flow ($2^\circ\text{C}/\text{min}$) followed by 2 hours at 500°C in air ($2^\circ\text{C}/\text{min}$). The protocol of surfactant remotion seems to play a key-role for the morphology of the product (table 1, fig. 1). The extraction with EtOH led to an alumina more various pore structured, with a wide and not too regular pore size distribution covering meso-microporous range. The thermal treatment led to a more defined structured compound, with a monomodal distribution of pores centred at about 4 nm of diameter.

Table 1: Morphological properties of aluminas used as support for catalysts

Al_2O_3	BET Surface Area (m^2g^{-1})	$V_{p.\text{tot.}}$ (mm^3g^{-1})	V_{up} (mm^3g^{-1})	$V_{\text{up}} / V_{p.\text{tot.}}$
commercial $\gamma\text{-Al}_2\text{O}_3$	144.9	60.71	12.75	0.21
<i>ALMN2</i>	348.1	284.0	82.29	0.29
<i>ALM7N2</i>	321.9	182.1	78.96	0.43

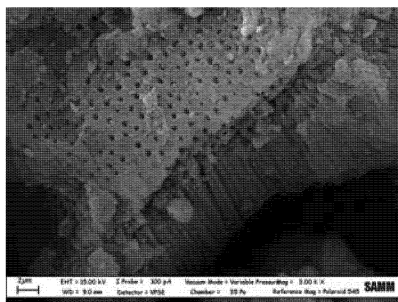


Figure 1: SEM image of the *ALMN2* sample

2.1 Catalysts preparation and characterization

Three catalysts have been prepared (*Ni-Acet15_N2H2*, *NiALMN2_N2H2*, *NiALM7N2_N2H2*). The precursor has been $\text{Ni}(\text{acac})_2$. *Ni-Acet15_N2H2* has been obtained *via* impregnation at 40°C for 4 h, using acetone as solvent and neutral activated alumina as support (powdered γ -alumina of high purity from Sigma Aldrich, table1). The solvent has been then evaporated under progressive vacuum (1 h, 700-300 mbar) at 40°C. After filtration and drying, the sample has been subjected to a thermal treatment (10°C/min till 450°C and 450°C for 2 h) in N_2 atmosphere (100 NmL/min) and to a reduction step (10°C/min until 500°C and 500°C for 1 h) in presence of H_2 (100 NmL/min). *NiALMN2_N2H2*, it has been prepared by a selective adsorption from solution: an impregnation step (4 h at 40°C) under stirring (acetone was the solvent and *ALMN2* alumina was the support), a filtration under vacuum, a washing steps at 40°C with acetone, a drying in air (100 mL/min) at 60°C for 4 h. The solid has been activated by a pyrolysis in N_2 at 450°C and a reduction in H_2 at 500°C. For *NiALM7N2_N2H2* the same protocol of preparation has been used, without a washing step and using *ALM7N2* as support. *Ni-Acet15_N2H2* shows a total surface area of 122.4 m²/g (micro-area: 20.1m²/g, non-micro area: 70.4 m²/g, micropores volume: 7.08 mm³/g). Ni content (ICP-OES elemental analysis by Perkin Helmer, Optima 2000DV) is 16.23 wt% . Fig. 2 and 3 show the DSC-TGA patterns (in air and in H_2 flow) of the catalyst after drying step and before the thermal treatment. It's possible to note that in presence of N_2 a greater weight loss occurs, and that is due to an endothermic process between 352°C and 472°C (max at 415°C). According to Von Heone, Charles and Hickam [14], this phenomena could be interrelated to the following reactions:

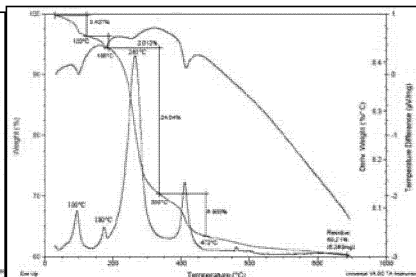
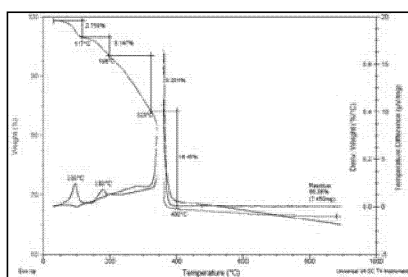
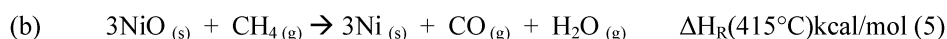
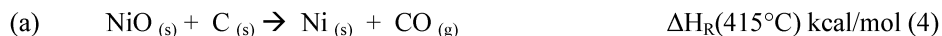


Figure 2: DSC-TGA in air atmosphere of *Ni-Acet15_N2H2* before thermal treatments

Figure 3: DSC-TGA in H_2 atmosphere *Ni-Acet15_N2H2* before thermal treatments

The thermal treatment in N_2 could decompose $Ni(acac)_2$ and lead to an almost complete autoreduction of NiO . It's an endothermic process and so it can minimize the sinterization and lead to smaller metallic Ni crystallites. Fig. 4 shows the XRD pattern (Bruker AXS-D8 Advance) of the catalyst after this treatment. Metallic Ni phase peaks are evident. A final thermal treatment in H_2 has been made. The weight loss was 0.5%, confirming that almost all nickel oxide had already been reduced. Fig. 5 shows the XRD pattern of the catalyst after treatment in N_2 and in H_2 . Ni peaks are evident but not intense: this could be due to the small aggregates. Fig 6 shows these Ni -aggregates. $NiALMN2_N2H2$ shows a surface area of $291\text{ m}^2/\text{g}$ and a Ni content of 4.86 wt%. $NiALM7N2_N2H2$ has a surface area of $274\text{ m}^2/\text{g}$ and a Ni content of 15.25 wt%.

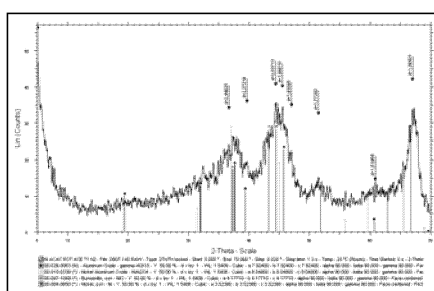
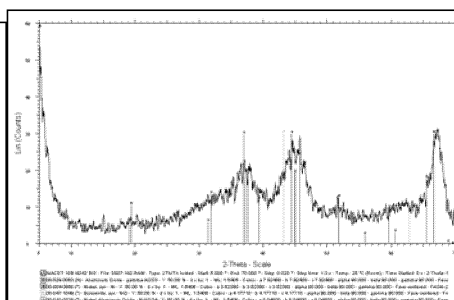
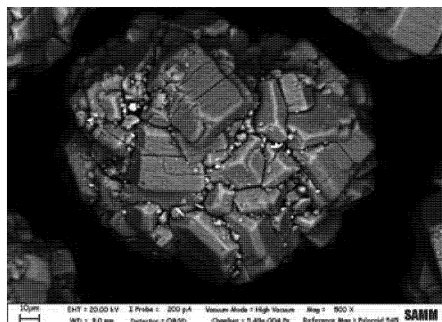
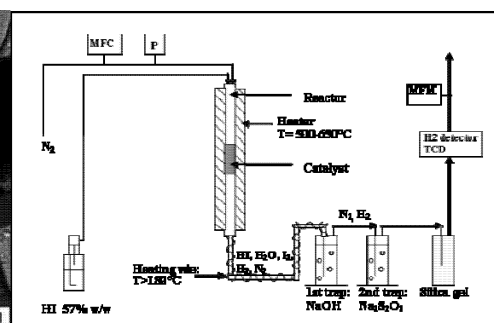
Figure 4: *Ni-Acet15_N2H2* XRD patternFigure 5: *Ni-Acet15_N2H2* XRD patternFigure 6: ESEM image of *Ni-Acet15_N2H2*

Figure 7: Experimental apparatus layout

3. Experimental apparatus

The catalytic tests have been carried in a quartz vertical fixed-bed reactor (I.D. 11.4 mm) placed in a thermostat-equipped oven and fed with 0.1 mL/min of HI aqueous solution at the azeotropic concentration (7.5 M, Sigma Aldrich) at $>136^\circ\text{C}$. The operative pressure is 1.3-1.4 bar and the operative temperatures are 500°C , 650°C and 700°C . The H_2 concentration in the output gas was determined by a TCD device (TCA 4000 - ADEV). An experimental apparatus layout is shown in fig. 7.

4. HI decomposition experimental results

4.1 Tests at 500°C

Fig. 8 shows the conversion of the HI decomposition reaction vs time in presence of *Ni-Acet15_N2H2* catalyst at 500°C . It decreases with time, starting from a maximum value

next to the thermodynamic value at this temperature. Comparing this trend with the result obtained in the previous work using *Ni-nitrate15* catalyst [1] which had a similar Ni content (14.55 wt%), it's possible to observe that the *Ni-Acet15_N2H2* conversion value is higher. The different precursor and the different preparation technique can improve the catalyst performance. It's interesting to compare fig. 8 with fig. 9 which shows the conversion in presence of *NiALM7N2_N2H2*. A difference occurred in the first 16 hours of experiment: *NiALM7N2_N2H2* didn't seem to deactivate. Fig. 10 shows the conversion obtained using *NiALMN2_N2H2*. The conversion started decreasing (2.2%) after 42 h. It's possible to conclude that a greater surface area and a greater pore volume of the support play a key-role on the activity of the catalyst. After a first step, however, a saturation of porous structure of alumina was reached and it was observed a decrease in conversion value, independently from the Ni content. Comparing the fig. 9 (*NiALM7N2_N2H2* at 500°C, 0.25g of catalyst mixed with 2.25g of SiC) and 11 (*NiALM7N2_N2H2* at 500°C, 0.5g of pure catalyst), it's noted that a larger amount of catalyst loaded to a longer stability in time.

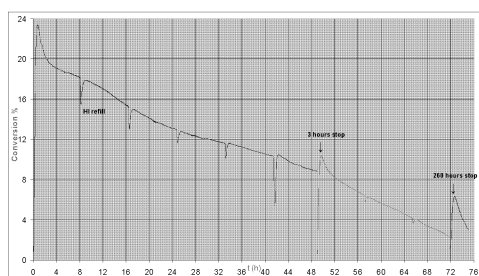


Figure 8: HI conversion vs time
(*Ni-Acet15_N2H2*)

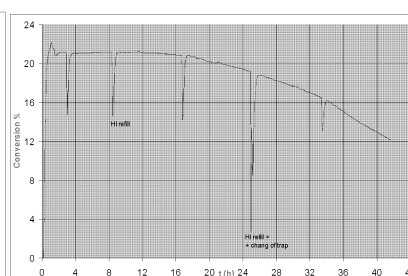


Figure 9 : HI conversion vs time
(*NiALM7N2_N2H2*)

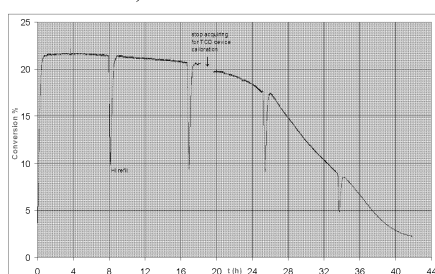


Figure 10 : HI conversion vs time
(*NiALMN2_N2H2*)

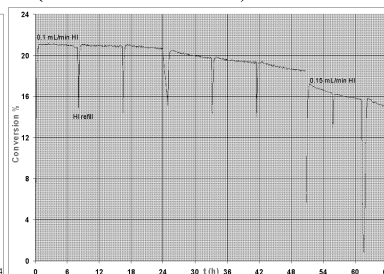


Figure 11: HI conversion vs time
(*NiALM7N2_N2H2*, 0,5 gr)

4.2 Long-time tests at 650°C and at 700°C

Fig. 12 shows the conversion in H_2 (*Ni-Acet15_N2H2*) vs time at 650°C. Comparing this figure with the fig. 9, it's possible to note that the conversion turned from 3% (for deactivated catalyst) to 21% (decreasing and reaching 16% after 48 h). Fig. 13 shows the conversion in H_2 (*NiALM7N2_N2H2*) at 700°C. It has been already tested at 500°C and it worked for 42 hours and it showed deactivation phenomena. The conversion value was about 27% and it remained constant during 67 h of test. So 700°C could be the proper temperature value working at for HI decomposition with a Ni-catalyst. This seems in agreement with the conclusions of the previous work [1], in which the NiI_2

formation as indicated as the main cause of the catalysts deactivation: 700°C is the NiI₂ decomposition temperature under an inert gas flow.

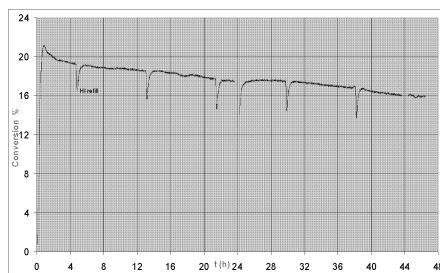


Figure 12: HI conversion vs time
(used *NiAcet15_N2H2*)

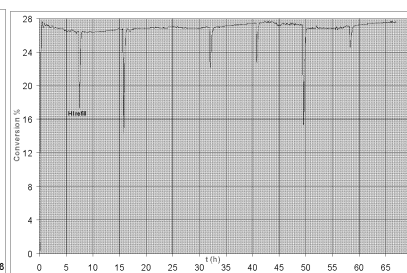


Figure 13: HI conversion vs time
(used *NiALM7N2_N2H2*)

4.3 Regeneration process of used catalysts

At the end of HI decomposition tests, the catalyst *Ni-Acet15_N2H2* has been cooled to room temperature under a N₂ flow and then it has been treated by a H₂ flow (100 mL/min) at 500°C (10°C/min) for 2 h. The tests, involving this 'regenerated' catalyst, showed a maximum conversion value < 1% and so this regeneration protocol didn't work. A longer regeneration process on *NiALMN2_N2H2* catalyst has been tested, doubling the time of exposure to the H₂ flow at 500°C (4 h). In this case the catalytic tests showed a maximum conversion value of 3%. It's possible to conclude that the reactivation of used Ni-catalysts in presence of H₂ doesn't work.

4.4 Analysis of the solid deposits at the bottom of the HI decomposition reactor

At the end of each test it has been observed a black solid deposit at the bottom of the reactor. In order to understand its chemical composition, the deposit formed during the test at 500°C in presence of *NiALM7N2_N2H2* has been recovered (0.01243g), treated with HCl (37%, 3 mL) and then with HNO₃ (69%, 1 mL) at room temperature. The ICP-AES analysis showed the presence of I₂ (75 wt%) and Ni (24 wt%). The molar ratio Ni/I₂ (0.69) was next to 0.5 (corresponding to NiI₂). So NiI₂ had been formed during the test maybe causing the catalyst deactivation.

Conclusion

Three Ni-based catalysts have been prepared, using *Ni(acac)*₂ as precursor and 3 different Al₂O₃ as support. The preparation protocol allowed to obtain small Ni crystallites, maximizing the active sites surface and the catalyst activity. The initial conversion values provided by the catalysts were close to the thermodynamic ones, but a progressive deactivation occurred. The catalyst surface properties played a key-role in the deactivation process: greater surface area and micropore volume implied a more constant conversion value during the first hours of the tests. Analyzing the solid deposit at the bottom of the reactor at the end of each experiment, it's possible to conclude that it could be the formation of NiI₂ the catalyst deactivation cause. Finally, the regeneration of used catalysts with a flow of H₂ (500°C) has been studied, but it didn't work. It's possible to conclude that Ni-catalysts are not suitable to be active on long-time scale HI decomposition. Maximizing surface area, using a support with a high micropore volume and raising Ni content, the catalytic activity can be improved.

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