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Nano-oxyhydride catalysts for hydrogen production from bioethanol at room temperature

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ABSTRACT

Well tuning the preparation, formulation and conditions applied, different series of nickel based nano-oxyhydride (Ni-Ce-O and Ni-Mg-Al-O based) catalysts were developed for the highly efficient and sustainable H₂ formation from ethanol in the presence of oxygen and water at room temperature. Once *in situ* treated in H₂ at adequate temperature, the nickel based mixed oxides become oxyhydrides, with the presence of hydrogen species of hydride nature in the anionic vacancies of the mixed oxides. The insertion into the solid of hydride species is well shown by Inelastic Neutron Scattering (INS). By taking advantage of the chemical energy released from the reaction between nano-oxyhydride catalysts and O₂, continuous complete conversion of ethanol specifically at 50°C (oven temperature), with simultaneously production of H₂, can be obtained. The sustainable process can be explained by a mechanism involving a heterolytic abstraction of hydride species from ethanol regenerating the oxyhydride catalyst.

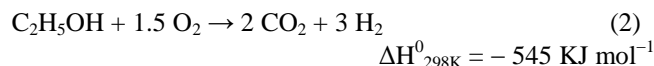
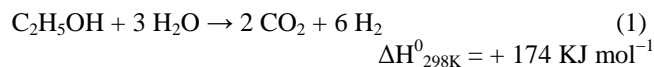
Keywords: Hydrogen, oxyhydride, catalyst, ethanol, nickel.

1 INTRODUCTION

The potential benefits of a hydrogen economy coming from renewable energy sources are creating a large consensus, it is important to find a way for obtaining “green” energy. Globally, the steam reforming of natural gas, especially methane, is still the most commonly used and the most economically competitive method for H₂ production. However, H₂ economy could be clean and sustainable only if it is produced from renewable sources and bioethanol obtained through biomass is a promising renewable source of hydrogen. In theory, hydrogen production from biomass or biomass derived liquids can be a carbon-emission free process and because of its low toxicity and ease of deliverability, ethanol lends itself very well to a distributed-production strategy. Besides, the wide-spread application of fuel cells become closer to reality, so

increased attention is focused on hydrogen production technologies.

So far, hydrogen has been produced from ethanol by steam reforming (SRE, Equation (1)), partial oxidation (POE, Equation (2)), oxidative steam reforming (OSRE), and autothermal reforming reactions [1-4]. The endothermic SRE reaction extracts more hydrogen atoms from ethanol and water, however, additional energy supply is needed. One alternative way of supplying heat is to add oxygen or air to the feedstock (OSRE) and simultaneously to burn a portion of ethanol.



The OSRE reaction is generally studied in the catalytic fixed-bed reactors [1-5] or the micro-channel membrane reactors [6]. The crucial factor is the development of highly efficient, stable and low-cost catalysts, that is, the design of the appropriate active sites which fulfil the above features of the OSRE reaction, especially the design of the non-noble metal catalysts. An ideal OSRE process desires to develop a catalyst working at low temperatures in order to build long life and safe reformers which can be employed for the portable applications.

Recently, we reported a novel route for the room temperature H₂ production over CeNiH₂O_Y nano-oxyhydride catalyst [5]. This promising technology can dramatically save energy by means of a smart combination of the exothermic reaction between the hydride species in the catalyst and O₂ (chemical energy) and the exothermic reaction between ethanol and O₂ (POE reaction). The CeNiH₂O_Y nano-oxyhydride catalyst was able to simultaneously activate ethanol with an oven fixed at 60°C, produce hydrogen, and provide hydride species to sustain the chemical reaction with O₂. It has to be precised that the reaction must be started at about 200°C. Moreover, it was shown that the effect of Ni content brings also interesting catalytic behaviors for the OSRE reaction. As a matter of

fact, we reported the $\text{CeNi}_x\text{H}_2\text{O}_y$ oxyhydrides as efficient and stable catalysts for H_2 production from ethanol with an oven fixed at 60°C [7].

It is today a major challenge to provide low cost catalysts able to efficiently break the C-C bond from bio-ethanol. Materials, such as catalysts or electrocatalysts that are able to activate fuels like H_2 , and alcohols are absolutely required for the development of new technologies [8, 9].

In the present study, we report H_2 formation on different nickel based oxyhydride catalysts from ethanol in the presence of oxygen and water. Correlations between catalytic activity and physico-chemical characterizations allow participating to the open debate on the active site and mechanism.

2 EXPERIMENTAL

The catalyst precursors were prepared by the co-precipitation method. The nano-oxides were obtained by calcination of the precursors at 500°C in the presence of air flow for 4 h [5, 7, 10, 11]. The metal loadings were analyzed by ICP-MS (CNRS–Service Central d’Analyses) (Table 1).

Inelastic neutron scattering (INS) experiments were carried out on the IN1 Lagrange spectrometer at the Institut Laue Langevin, Grenoble. 36 g of the solid was placed in a stainless steel container and *in-situ* treated in high purity H_2 (10 h).

The catalytic reaction was performed under atmospheric pressure in a fixed-bed up-flow quartz reactor (inner diameter 4 mm) fitted in a programmable oven [5, 7]. The catalyst (0.03 g) was previously *in situ* treated in pure H_2 at 250°C for Ni-Ce-O catalyst and at 450°C for Ni-Mg-Al-O catalyst for 10 h. The reactant mixture (molar ratio: $\text{EtOH}/\text{H}_2\text{O} = 1/3$) was injected into a heating chamber (ca. 140°C) by HPLC pump to the flow of $\text{O}_2\text{-N}_2$ mixture (60 mL min^{-1}). The gas stream of $\text{EtOH}/\text{H}_2\text{O}/\text{O}_2/\text{N}_2=1/3/1.6/1.3$ was then fed to the reactor. The outlet gases were analyzed online by GC (TRACE GC ULTRA) equipped with a TCD and a FID detector. To be noticed, the reactants were introduced in a specific order, and O_2 must be added in the last to avoid the immediate re-oxidation of the oxyhydride. After all the reactants were introduced, the reaction was activated at a certain temperature, depending on the ability of the oxyhydride catalyst to react with O_2 . The heat of the oven was reduced as soon as the measured reaction temperature started to increase drastically, and the variation in the reaction temperature was recorded.

3 RESULTS AND DISCUSSION

Different nickel based nano-oxyhydride (Ni-Ce-O and Ni-Mg-Al-O based) catalysts are developed. The selected pre-treatment temperature in H_2 is important for generation of an oxyhydride. The influence of the pretreatment temperature (T_T) on ethanol conversion in SRE conditions

has been studied previously. On cerium nickel based compounds an optimum T_T has been reported at 250°C [12, 13], while on Ni-Mg-Al-O compound it has been shown that when increasing T_T an increase of the conversion can be obtained however, carbon formation increases also, therefore a good compromise was obtained for a T_T at 450°C [10, 11].

Catalyst	Ni [wt%]	S_{BET} [$\text{m}^2 \text{g}^{-1}$]
Ni-Ce-O	21	110
Ni-Mg-Al-O	62	196

Table 1. Ni content and specific area of the catalysts

Once *in situ* treated in H_2 at adequate temperature, the nickel based mixed oxides (Table 1) become oxyhydrides, with the presence of hydrogen species of hydride nature located in the anionic vacancies formed in the mixed oxides. The insertion into the solid of hydride species is well shown here by Inelastic Neutron Scattering (INS) [14, 15]. The H_2 treatment generates an increase of the INS spectrum level as well as the emergence of new peaks associated to hydrogen vibration bands. Importantly, the spectrum level is proportional to the concentration of hydrogen. The hydrogen species with the hydride nature appear clearly on Ni-Ce-O compound after a treatment in H_2 at 250°C (Figure 1) and on Ni-Mg-Al-O compound after a treatment in H_2 at 450°C (Figure 2). It has to be remarked that after treatment in vacuum at 200°C (to eliminate physisorbed water) some hydrogen species are always present in the compounds, corresponding to hydroxyl groups. The vibration bands obtained at about 30, 50 and 77 meV were assigned to hydroxyl groups on the CeNi_xO_y nano-compounds [5]. After treatment in H_2 , main new peaks are observed at around 60 meV and 110 meV for Ni-Ce-O compound and at around 76, 98 and 208 meV for Ni-Mg-Al-O, even if the spectra are complex contribution from the ternary Mg-Al-Ni system. It has been reported that magnesium hydride presents two peaks in the range between 60-80 meV [16], while aluminum hydride leads to a large spectrum with several peaks between 76 and 117 meV [17], and nickel hydride shows broad bands at around 100 and 200 meV [18].

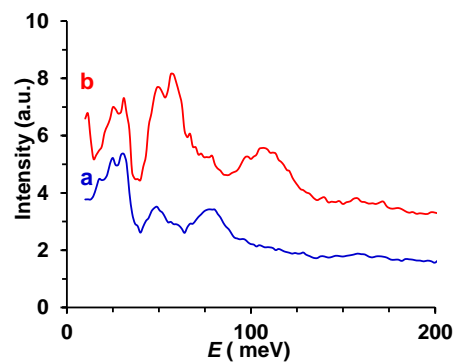


Figure 1: INS spectra of Ni-Ce-O a) treated in vacuum at 200°C for 2 h and b) in H_2 at 250°C for 10 h.

Hydrogen can be mainly heterolytically dissociated on an anionic vacancy and an O^{2-} species of the catalyst [Equation (3)].

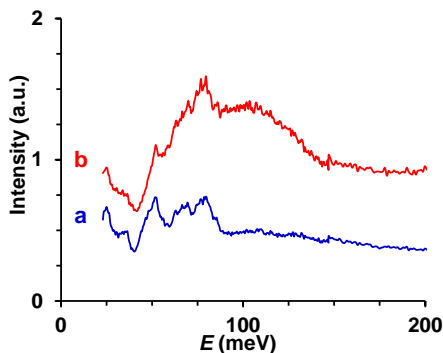
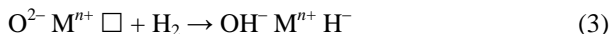


Figure 2: INS spectra of Ni-Mg-Al-O a) treated in vacuum at 200°C for 2 h and b) in H_2 at 450°C for 10 h.

The catalyst is first *in situ* pre-treated in H_2 in order to form the nano-oxyhydride, then it is studied for H_2 production in the presence of ethanol, water and O_2 (molar ratio: $EtOH/H_2O/O_2/N_2 = 1/3/1.6/1.3$). The oven temperature is fixed at only 50°C whereas the reaction temperature is measured and reported. The reaction must be initiated at about 200°C, then the temperature quickly increases during an induction period of a few minutes (around 3 min). The heating can be then lowered and only a small extra energy is needed to realize the reaction. The measured reaction temperature is reported at the stable state.

Ethanol and oxygen are completely converted on the catalysts (Figures 3 and 4). Only small quantities of CH_4 and CH_3CHO are detected in outlet gases (< 1%). In complement to the exothermic partial oxidation reaction of ethanol, by taking advantage of the chemical energy released from the reaction between hydride species stored in the nano-oxyhydride catalysts and O_2 , continuous complete conversion of ethanol specifically at 50°C (oven temperature), with simultaneously production of H_2 , can be obtained. Figure 3 shows the results obtained on the Ni-Ce-O based nano-oxyhydride, with a H_2 formation of about 46% (mol%) relative to all the gas phase products (dry basis). The other products analyzed are mainly CO_2 (41%) and CO (12%). The oven temperature is fixed at 50°C and the measured reaction temperature is much higher at 330°C. Figure 4 shows that relatively similar results can be obtained on a Ni-Mg-Al-O based nano-oxyhydride catalyst. A H_2 formation of about 45% is obtained with mainly CO_2 (45%) and CO (10%). The oven temperature is fixed at 50°C while the measured reaction temperature is at 260°C.

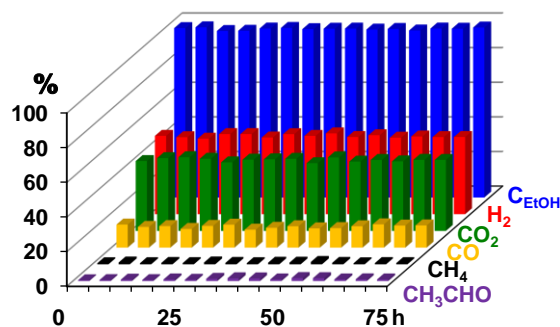


Figure 3: Ethanol conversion and products distribution on Ni-Ce-O based nano-oxyhydride. The reaction mixture is $EtOH/H_2O/O_2/N_2 = 1/3/1.6/1.3$. The oven temperature is fixed at 50°C and the measured reaction temperature is at 330°C.

The catalysts exhibit remarkable stability after at least 75 h of reaction, even if filamentous carbon deposition is found after the reaction. The conversion is increased significantly by the addition of O_2 into the reactant mixture. For comparison, we have reported a high and stable activity (5 h) at 250°C in the SRE conditions (14 mol.% EtOH) with ethanol conversion at 50% and H_2 formation at 55% over high Ni content Ni-Mg-Al-O catalyst (0.05 g).

H_2 and CO_2 are the ideal products from SRE and POE processes [Equations (1) and (2)], and CO is the only byproduct. The sum of acetaldehyde and methane is lower than 1%. However, solid carbon is also formed.

Dehydrogenation of ethanol produces acetaldehyde and H_2 [Equation (4)], whereas decomposition of ethanol (and/or acetaldehyde) produces CO , methane and H_2 [Equation (5)] and total decomposition leads to CO , H_2 and carbon [Equation (6)]. Water-gas shift reaction favored at low temperature allows the transformation of CO [Equation (7)]. In the presence of O_2 , partial oxidation reactions take place. POE may be considered as a combination of partial oxidation to syngas coupled with CO oxidation [2].



Acetaldehyde has been proposed as an important reaction intermediate in SRE and OSRE, and the abstraction and dissociation of hydrogen species from ethanol (dehydrogenation) through C–H rupture is usually remarked as the rate-determining step. As we have proposed for the heterolytic dissociation of H_2 [Equation (3)], an active site involving an anionic vacancy and an O^{2-} species of the solid can be envisaged for the heterolytic dissociation of ethanol [Equation (8)].

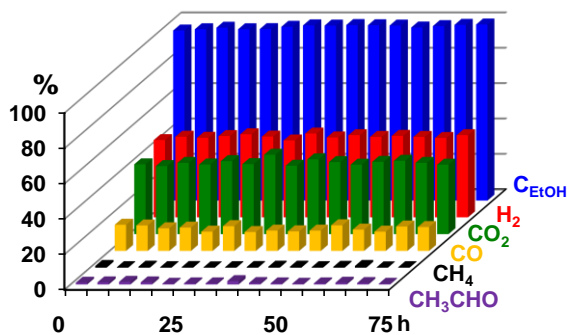
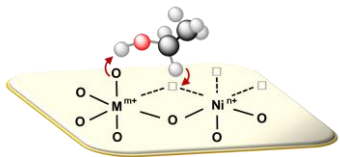


Figure 4: Ethanol conversion and products distribution on Ni-Mg-Al-O based nano-oxyhydride. The reaction mixture is EtOH/H₂O/O₂/N₂= 1/3/1.6/1.3. The oven temperature is fixed at 50°C and the measured reaction temperature is at 260°C.

The present result is a major advance in the field, because conversion of concentrated ethanol into H₂ production with low energy consumption is of value in the practical use.

Different physicochemical techniques were used to characterize the catalysts and carbon formed. The active nickel species are found in strong interaction with other cations. Finally, to explain the sustainable process, an active site involving an anionic vacancy and an O²⁻ species of the solid can be envisaged, as proposed in Scheme 1, with abstraction of hydride species from ethanol and regeneration of the oxyhydride catalyst.



Scheme 1: Activation of ethanol

4 CONCLUSION

Hydrogen has been produced from ethanol in the presence of oxygen and water. Well tuning the catalyst preparation, formulation and Ni content, as well as the activation procedure and the reaction conditions allows obtaining a high and stable activity at room temperature (oven) even if some solid carbon is formed. It appears that the active nickel species are in strong interaction with other cations. An active site involving cations and anionic vacancies is proposed leading to a mechanism involving heterolytic abstraction of hydride species from ethanol.

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