Highly-loaded well-dispersed ex-hydrotalcite Mg2AlNi12HZOY oxyhydride catalysts for sustainable hydrogen production from steam reforming and oxidative steam reforming of ethanol

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PURPOSE OF THE ABSTRACT
At the international level hydrogen has been proposed as a future clean energy source that could contribute to the reduction of global dependence on fossil fuels, greenhouse gas emissions and atmospheric pollution. H2 production from bio-ethanol is regarded as an environmentally-friendly and sustainable-efficient route [1]. Moreover, the wide-spread application of fuel cells become closer to reality, and ethanol can be sent directly to fuel cells as safe fuel. Therefore, increased attention is focused on H2 production technologies. Steam reforming (SRE) and oxidative steam reforming of ethanol (OSRE) are widely practiced thermal-chemical technology to convert ethanol into H2 production. Worldwide efforts are nowadays devoted to the development of more active and more stable catalysts. Providing low cost catalysts able to efficiently break the C-C bond is an international major challenge [2]. Preparation of stable nanoparticles in high proportion has huge applications not only in catalysis. Thermal treatment of Mg-Al-Ni hydrotalcite-like compounds allowed synthesis of highly-loaded well-dispersed multi-component Mg2AlNi12XOY nano-composites [3]. Once in situ treated in H2 at adequate temperature, the mixed oxides 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 by Inelastic Neutron Scattering (INS). The H2 treatment generates an increase of the INS spectrum level as well as the emergence of new peaks associated to hydrogen vibration bands (Figure 1) [4]. The sustainable process can be explained by a mechanism involving a heterolytic abstraction of hydride species from ethanol regenerating the oxyhydride catalyst. An active site involving an anionic vacancy and an O2- species of the solid can be envisaged for heterolytic dissociation of ethanol as it has been proposed for heterolytic dissociation of H2 [5,6]. In SRE (Figure 2A) the Mg2AlNi12HZOY catalyst allowed total conversion of ethanol at as low as 250 oC with the production of H2, CO2 and CH4, when using a low concentration of ethanol (EtOH: 1% in mol.). A CO-free stable H2 production (125 hours of lifetime) at 3 mol/mol was obtained at 300 oC which corresponded to 100% of H2 yield in total decomposition of ethanol to hydrogen. Working at a higher concentration of ethanol (EtOH: 3%), total conversion of ethanol was obtained at only 450 oC. A high H2 yield at 4.8 mol/mol was achieved at 650 oC, one of the best ever reported for the low-cost catalysts. In OSRE (Figure 2B) the Mg2AlNi3HZOY catalyst provided a
full conversion of concentrated ethanol (EtOH: 14%, 75 hours of lifetime minimal) at only 50 oC (oven-heating) with a H2 formation of about 45% (mol%) relative to all the gas phase products (dry basis). The other products analyzed were mainly CO2 (41%) and CO (13%). Both catalytic processes were stable even if filamentous carbon deposition was found after reaction.
FIGURE 1
INS & active site modeling
INS spectra of Mg2AlNiXHZOY (with H2 treatment at 450 oC) after subtraction of spectra of Mg2AlNiXOY (with vacuum treatment at 200 oC). Active site proposition for transformation of ethanol to H2 over Mg2AlNiXHZOY nano-oxyhydrides.

FIGURE 2
Catalytic performances
(A) SRE on the Mg2AlNi12HZOY catalyst and (B) OSRE on the Mg2AlNi3HZOY catalyst.

KEYWORDS
oxyhydride | hydrogen | nickel | ethanol

BIBLIOGRAPHY