Experimental Report

16/05/2013

Proposal:	**7-05-397**	**Council:**	4/2012	
Title:	Analysis by INS of hydrogen species in Mg-Al-Ni based mixed oxides			
This proposal is continuation of: 7-05-362				
Researh Area:	Chemistry			
Main proposer:	**DUHAMEL louise**			
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Samples:	Mg2NixAl			

Instrument	Req. Days	All. Days	From	To
IN1	6	4	02/11/2012	06/11/2012

Abstract:

Our last INS experiments helped us to successfully develop the CeNiHZOY oxyhydride compound, an exceptional catalyst that totally converts ethanol (biomass) at room temperature and produces H2 in the presence of water and oxygen. H2 is produced from ethanol in a sustainable way by taking advantage of the chemical energy brought by the reaction between hydride species from the nano-oxyhydride catalyst and O2. (Angew. Chem. Int. Ed. 50 (2011) 10193)
In the present study we wish to analyze Mg-Al-Ni hydrotalcite type catalysts that present also very high catalytic activities for the production of hydrogen from ethanol. It is therefore very interesting to study the existence and nature of hydrogen species that can be inserted into these solids after treating in H2. As a matter of fact the activation in H2 is a prerequisite condition to observe activity at low temperature.

Analysis by INS of hydrogen species in Mg-Al-Ni based mixed oxides

In our laboratory, it was shown that some materials presenting very good catalytic activities such as cerium and nickel based mixed oxides are able to store very high quantities of catalytic hydrogen. This phenomenon was related to the presence of anionic vacancies allowing hydride species formation and storage. Inelastic neutron scattering (INS) was used to obtain information on the nature of hydrogen species.[1-3] H_2 treatment modifies the peaks related to hydroxyl groups (H^+) and generates the emergence of new peaks. In particular, a large band at about 480 cm^{-1} is observed on the H_2 treated solids, due to the insertion of hydride species (H^-). These experiments helped us to successfully develop the $CeNiH_ZO_Y$ oxyhydride compound, an exceptional catalyst that totally converts ethanol (biomass) at room temperature and produces H_2 in the presence of water and oxygen.[4] $Mg_2AlNi_XO_Y$ catalysts present also high catalytic activities for the production of hydrogen from ethanol. It is therefore very interesting to study the existence and nature of hydrogen species that can be inserted into these solids after treating in H_2. As a matter of fact the activation in H_2 is a prerequisite condition to observe activity at low temperature.

Experimental

The $Mg_2AlNi_XO_Y$ mixed oxides were prepared by co-precipitation, dried and calcined in air at 500 °C during 5h. For each experiment, 36 g of solid were placed inside inox steel container, and the treatment applied in H_2 (10 h) was performed using high purity gas. INS-experiments were carried out at 10 K at the IN1 Lagrange.

Results and discussion

The $Mg_2AlNi_XO_Y$ compounds have been analysed after treatment in vacuum (200 °C, 2h) and after treatment in H_2 at 450 °C. Some hydroxyl groups are present in the compounds after calcination and pumping in vacuum, as shown Fig. 1 presenting the INS spectra of the $Mg_2AlNi_XO_Y$ compounds after treatment in vacuum at 200 °C. The spectrum level decreases with the increase of Ni content. It appears that in the oxidized state, the concentration of hydrogen decreases when Ni content increases. When x = 1, ($Mg_2AlNi_1O_Y$ compound) the spectrum is complex, broad and large with main peaks at about 645 cm^{-1} and 822 cm^{-1}, while when x= 3 the peaks are found at 423 cm^{-1} and 641 cm^{-1}. When x= 12, peaks at 419 cm^{-1}, 560 cm^{-1} and 640 cm^{-1} can be reported. It is clearly seen that the broad peak at about 822 cm^{-1} decreases drastically when Ni content increases. Therefore, it appears that two peaks at about 420 cm^{-1} and about 640 cm^{-1} are present on all the compounds but the peak at 420 cm^{-1} seems to increase with Ni content, while the peak at about 640 cm^{-1} seems to decrease when Ni content decreases.

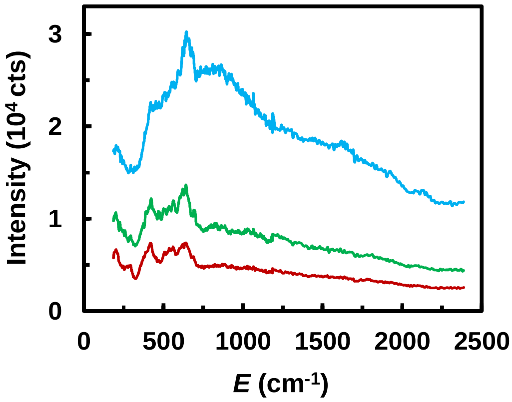

Figure 1: INS spectra of $Mg_2AlNi_XO_Y$ treated in vacuum at 200 °C. x = 1 (blue), x= 3 (green), and x= 12 (red).

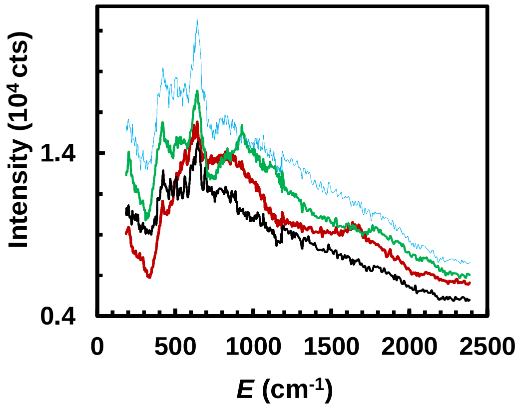

Figure 2: INS spectra of $Mg_2AlNi_XO_Y$ treated in H_2 at 450 °C. x = 0 (black), x = 1 (blue), x= 3 (green), and x= 12 (red).

After treatment in H_2 at 450 °C, the INS spectra of the $Mg_2AlNi_XO_Y$ compounds vary, showing modification of the compounds. Exceptionally, the spectrum level of the $Mg_2AlNi_1O_Y$ compound decreases showing that the solid contains less hydrogen after treatment in H_2 (Fig. 3), certainly due to a loss of hydroxyl groups at 450 °C. The spectrum presents main peaks at 420 cm^{-1}, and 640 cm^{-1}, while when x= 3 the peaks are observed at 419, 641, and 927 cm^{-1} and when x= 12, peaks at 419, 641 cm^{-1} can be reported. For comparison the Mg_2AlO_Y presents two peaks at 423 $cm^{-1}$and 645 cm^{-1}. Therefore, all compounds present common peaks at about 420 cm^{-1} and 645 cm^{-1} related to the presence of Mg_2AlO_Y.

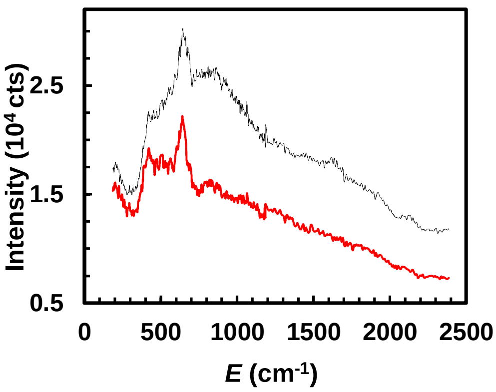

Figure 3: INS spectra of $Mg_2AlNi_1O_Y$ treated in vacuum at 200 °C (2h) (black) and treated in H_2 at 450 °C (red).

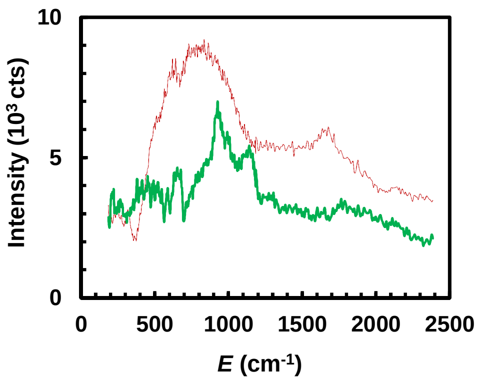

Figure 4: INS spectra of $Mg_2AlNi_XO_Y$ treated in H_2 at 450 °C. x = 3 (green), and x = 12 (red). (INS spectrum of the solid treated in vacuum at 200 °C is subtracted).

For better visualisation of the new type of hydrogen species inserted into the solids in H_2 at 450 °C, the spectrum obtained with the corresponding compound in the oxidized state is subtracted to the spectrum obtained over the H_2 treated solid (Fig. 4). The $Mg_2AlNi_3O_Y$ solid presents clearly two new peaks at about 927 cm^{-1} and 1140 cm^{-1} related to new hydrogen species. The

$Mg_2AlNi_{12}O_Y$ compound presents a very broad peak at about 780 cm^{-1}. It seems also that there is a small common new peak at about 600 cm^{-1} for the two compounds.

Finally, INS experiments allow to clearly evidence that the $Mg_2AlNi_XO_Y$ mixed oxides contain hydrogen species after calcination and *in situ* treatment in vacuum at 200 °C. These hydrogen species correspond to hydroxyl groups present in the nano-compounds. Moreover, the treatment in H_2 at 450 °C leads to an insertion of new hydrogen species into the solids and the $Mg_2AlNi_XO_Y$ nano-compounds (with $x > 1$) are transformed into nano-oxyhydrides. These nano-oxyhydrides contain hydrogen species of hydride nature as well as hydrogen species related to hydroxyl groups.

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1. a) Observation by neutron spectroscopy of metal-hydrogen species in mixed oxides hydrogen reservoirs. ILL report N°7-05-269, (2006). b) INS characterization of catalytic hydrogen storage in CeZr0.5NiXOY and CeNiXOY mixed oxides, N°7-05-298 (2007).c) INS characterization of hydrogen species in cerium and nickel based oxyhydrides, N° 7-05-334 (2009). d) Analysis by INS of hydride species in cerium and nickel based mixed oxides N° 7-05-362 (2011)

2. L. Jalowiecki-Duhamel**,** S. Debeusscher, H. Zarrou, A. D'Huysser, H. Jobic, E. Payen. Catal. Today 138 (2008) 266-271.

3. L. Jalowiecki-Duhamel, S. Debeusscher, H. Jobic and E. Payen. Int. J. Nuclear Hydrogen Production and Applications 2 (2009) 148-158

4. C. Pirez, M. Capron, H. Jobic, F. Dumeignil, L. Jalowiecki-Duhamel. Angew. Chem. Int. Ed. « Very important paper » 50 (2011) 10193-10197.