

## TECHNICAL COMMUNICATION

# SOME COMMENTS ON MODES OF ACTIVATION OF $\text{LaNi}_5$ AND $\text{CaNi}_5$ ALLOYS FOR HYDROGEN STORAGE

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**Abstract**—Intermetallics used for hydrogen storage purposes require prior activation. Mild activation conditions are sufficient for  $\text{AB}_5$  type intermetallics like  $\text{LaNi}_5$  and  $\text{CaNi}_5$ , as compared to other intermetallics used for the purposes of hydrogen storage. In this communication a model for the activation process is proposed for the behaviour of  $\text{LaNi}_5$  and  $\text{CaNi}_5$  alloys.

### INTRODUCTION

The surface of hydrogen storage  $\text{AB}_5$  type intermetallics has been examined by various workers [1] with a view to developing suitable activation procedures for these materials. The important steps in the hydriding of metals, alloys or intermetallics are the adsorption and dissociation of molecular hydrogen into atomic hydrogen on the surface. Many clean transition metal surfaces have this capability of dissociating hydrogen, but lose this property upon oxidation. The published results on  $\text{AB}_5$  type alloys [2] show that upon exposure to air both constituent metals of the alloys are oxidized at the surface leading to the formation of their respective oxides, though of different compositions. This oxidation process thus necessitates the development of suitable activation procedures for these alloys for use in hydrogen storage applications. The purpose of this communication is to propose a model for the activation of  $\text{AB}_5$  type alloys especially with respect to  $\text{LaNi}_5$  and  $\text{CaNi}_5$ .

### EXPERIMENTS AND DISCUSSION

The necessary XPS and XAES data were obtained using an ESCALAB MK II instrument. The experimental conditions and the procedures employed are described elsewhere [3]. The data summarized in Table I show that the surfaces of the air-exposed samples of these alloys are oxidized. Though in the top layers, the hydroxide species of the A elements are discernible, the oxide layers alone are seen on sputtering for short periods. The oxidized nature of nickel is deduced from the satellite features (861.5–862.5 eV) as well as from the position of  $\text{Ni}(2p_{3/2})$  emission. The Ni (LMM) Auger transitions also reveal the passivated nature of nickel.

The presence of these readily formed easily reducible ( $\text{NiO}$ ) and non-reducible ( $\text{La}_2\text{O}_3$  and  $\text{CaO}$ ) oxides on the surface obviously prohibit hydrogen absorption

owing to impeded hydrogen dissociation on the oxide surface or to slow hydrogen permeation through these protective layers. The rates of kinetic processes of hydrogen sorption are also considerably decreased. The dissociation of molecular hydrogen, the diffusion of hydrogen atom/molecule and the association of hydrogen atoms are important steps in the hydrogen storage process and hence the surface should contain active surface sites. It is well known that clean surfaces of many transition metals are able to adsorb hydrogen dissociatively and desorb it associatively [4]. Therefore, the surface should be activated in order to get the metal clusters which are active for the reaction under interest. However, in the present instance the nickel oxides formed on the surface can be easily reduced and activated by hydrogen even at room temperature to produce the active metal clusters [5, 6].

After activation, the resultant alloy surface produced may be described as a supported-metal system, namely,  $\text{Ni}/\text{La}_2\text{O}_3$  and  $\text{Ni}/\text{CaO}$ , respectively, on  $\text{LaNi}_5$  and  $\text{CaNi}_5$ . Of the many reasons for the supported metal catalyst use, none is more important than high degree of dispersion of the metal which can be achieved with comparative ease. Moreover, in the present case it is expected that the supported metal oxides may be homogeneously distributed (because of the *in situ* decomposition of the alloy and the subsequent oxidation) across the surface of the support. The higher dispersion in the case of alloys is responsible for the higher catalytic activity observed compared to the conventionally prepared supported catalysts [7]. The support may act purely as a dispersing agent and/or might itself promote reduction.

During activation, the oxide (reducible oxides, namely nickel oxide) and hydrogen come into contact, the reaction (reduction) starts and after some time, the first metal nuclei of the solid product form. It is considered that these can then dissociate and activate hydrogen so

Table 1. Summary of XPS data on LaNi<sub>5</sub> and CaNi<sub>5</sub> alloys

Sample	Surface species	Line probed	Binding energy (eV)		Satellite	Kinetic energy (eV)	
			Main peak	Satellite		Ni (LMM)	
LaNi <sub>5</sub> Air exposed	La(OH) <sub>3</sub>	La 3d <sub>5/2</sub>	836.0	840.1*	~848.0†		
	La <sub>2</sub> O <sub>3</sub>		834.8	838.5*	~848.0†		
	NiO	Ni 2p <sub>3/2</sub>	854.4	861.9	—	862.2‡	843.2‡
	Ni <sub>2</sub> O <sub>3</sub>			862.5§	—	844.5‡	
	Ni(OH) <sub>2</sub>			862.5§	—	842.0‡	
Sputtered 1 h	La	3d <sub>5/2</sub>		~843.0	~854.0		
	Ni	2p <sub>3/2</sub>	852.8	858.4¶		846.4**	
CaNi <sub>5</sub> Air exposed	Ca(OH) <sub>2</sub>	2p <sub>3/2</sub>	347.6				
	CaO		347.0				
	NiO	2p <sub>3/2</sub>	854.3	861.5††		846.0	843.2
	Ni <sub>2</sub> O <sub>3</sub>		855.5	862.7§		844.0	
	Ni(OH) <sub>2</sub>		856.5	862.7§		842.0	
Sputtered 1 h	Ca	2p <sub>3/2</sub>	345.7				
	Ni	2p <sub>3/2</sub>	852.8	858.4¶		846.3	

\*Normally observed satellite and is assigned to O 2p La 4f charge transfer transition.

†Broad weak feature due to O 2p La 3d charge transfer termed as double shake up process.

‡Broad feature characteristic of higher valent nature of Ni species.

§Broad lines due to overlap of both Ni<sub>2</sub>O<sub>3</sub> and Ni(OH)<sub>2</sub>.

||Energy loss features characteristic of La metal.

¶Energy loss feature characteristic of metallic Ni.

\*\*Sharp peak characteristic of metallic Ni.

††Monopole charge transfer satellite characteristic of NiO.

that the process of reduction is "autocatalytic". The reduction is called autocatalytic when reduced metal formed in the early stages of reduction catalyse the reduction by hydrogen activation. The NiO and CuO formed are known examples of promoters of such a process [8]. In the presence of either support or promoter these oxides still reduce with ease. However, it should be mentioned here that the reduction may either be hindered or promoted depending upon the nature of the oxide and the support. Hence, supported-metal oxides may exhibit different reduction behavior compared with unsupported oxides.

The hydrogen atoms formed by the dissociation of molecular hydrogen on metal particles may easily migrate to another phase which has hydrogen acceptor sites, namely, the support. This process is often called "Hydrogen spill-over" [9]. The spilt-over hydrogen may reside on the surface of the support or second phase, diffuse into it and lead to its partial reduction. In each of these states, spilt-over hydrogen has important implications. For example, it has been claimed that it can increase the catalytic activity of the support or the second phase.

It has been reported in the literature that the amount of hydrogen adsorbed on a nickel catalyst was increased by the combination with La<sub>2</sub>O<sub>3</sub> [10, 11] as a result of hydrogen-spillover [9] where Ni/La<sub>2</sub>O<sub>3</sub> acts as the hydrogen acceptor. Similar results occur where Ni/La<sub>2</sub>O<sub>3</sub> acts as the hydrogen acceptor. Similar results have also been observed for NiO on La<sub>2</sub>O<sub>3</sub> modified with alumina [12]. This is a reflection of the easy reducibility as evidenced by the percentage of reduction and metal surface area.

Therefore, it can be concluded that the surface oxides formed on LaNi<sub>5</sub> may behave like metal-supported

systems (Ni/La<sub>2</sub>O<sub>3</sub>) and hence the foregoing arguments can account for the observed rapid kinetics after the low mild activation requirements. In a similar way the behaviour of CaNi<sub>5</sub> alloy also follows an analogous pattern to the model proposed for LaNi<sub>5</sub>, where typically Ni/CaO is formed which in turn enhances the activity and requires little or no activation treatment. This explanation is further supported by the fact that when CaO, SnO and BaO modified alumina are used as supports, they inhibit oxidative sintering of iridium [13]. Probably, CaO is more preventive of nickel from sintering than is La<sub>2</sub>O<sub>3</sub> in the case of LaNi<sub>5</sub>. At present this is only a conjecture. The behaviour of nickel and iridium could also be different. However, this explains why CaNi<sub>5</sub> is more easily activated than LaNi<sub>5</sub>. It may be noted that analysis shows that more nickel is found on the surface of CaNi<sub>5</sub> than on LaNi<sub>5</sub> [14].

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