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EXAFS AND NES STUDIES OF RARE EARTH AND TRANSITION METAL CATALYSTS

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RESUME

Une série de composés intermétalliques RNi_x ($R = La, Ce$; $x = 2$ ou 5) et $CeNiAl$ ainsi que les hydrures stables RNi_2H_4 et $CeNiAlH_{3,3}$ ont été testés dans la réaction d'hydrogénation du monoxyde de carbone. Ces composés présentent une période d'activation qui a pu être reliée à la décomposition des composés initiaux en un système nickel sur oxyde de terre rare. Les conditions d'activation et l'activité catalytique dépendent fortement de la composition initiale et du taux de décomposition de l'intermétallique ou de l'hydrure, alors que la sélectivité ne varie pas.

ABSTRACT

A series of RNi_x ($R = La, Ce$ and $x = 2$ or 5) and $CeNiAl$ intermetallics and stable RNi_2H_4 and $CeNiAlH_{3,3}$ hydrides have been tested in CO hydrogenation. The observed increase of activity with time on stream has been correlated to the decomposition of the compounds into nickel supported on rare-earth oxide. Catalytic activity and time and temperature conditions of activation are related to the initial composition and the transformation of the compounds, whereas selectivity is unchanged.

1 - INTRODUCTION

Recently a great number of catalytic studies has been undertaken on intermetallic compounds (1, 4). In this framework we have studied a series of RNi_x ($R = La, Ce$ and $x = 2$ or 5) and $CeNiAl$ alloys in carbon monoxide hydrogenation. Moreover as RNi_2 and $CeNiAl$ form stable hydrides (V. PAUL-BONCOUR et al. submitted to J. Less Common Metals), these hydrides were also tested in catalytic reaction in order to observe the possible role played by the stored hydrogen.

However an increase of activity with time on stream was observed for both intermetallics and hydrides. Characterization of these compounds after catalytic reaction by X-ray diffraction (XRD) gave evidence of their partial decomposition into nickel metal as it was previously observed for RNi_5 ($R = La, Ce$) intermetallics (1). In order to correlate the catalytic properties and this decomposition, each sample was characterized before and after reaction by XRD and X-ray absorption (XAS).

Experimental

The intermetallic compounds were prepared by induction melting of pure components under vacuum (5). Their homogeneity, stoichiometry and structure were checked by metallographic examination, electron microprobe analysis and X-ray powder diffraction.

Before use, all the alloys were powdered and sifted in a gloves box under purified argon. Catalytic tests were carried out in a dynamic fixed bed reactor described in (1) at atmospheric pressure with a $\text{CO}:\text{H}_2$ ratio of 1. EXAFS spectra at Ni-K-edge and XANES spectra at Ce-L_{III} edge have been collected at LURE using the synchrotron radiation provided by D.C.I ring. Ce M_{IV-V} absorption spectra were recorded by photoelectron yield on ACO.

2 - RESULTS AND DISCUSSION

Catalytic properties

All the compounds exhibit an increase of activity during time on stream, as it is presented on figure 1 for CeNi₂ and CeNiAl alloys and their hydrides. Different time and temperature conditions are required to activate the compounds as presented on table 1. All the compounds show the same activation energy ($E_A = 25$ kcal/mole) and the same variation of selectivity as a function of CO conversion. This means that no electronic factors are involved in the catalytic properties of the various compounds and that the difference of activity, at a given temperature, is related to the number of active sites.

Characterization

The different phases determined by X.R.D. after catalytic reaction are reported on table 1.

Comparison of the EXAFS spectra at Ni K-edge of the compounds before and after reaction with FCC Nickel clearly show the transformation into nickel. Nevertheless in most case the signal is smaller than that of the standard Ni foil as it is observed in the Fourier transform (F.T.) of CeNiAlH₃ (figure 2). This difference as been interpreted as due to a mixing of nickel particles and undestroyed intermetallic or hydride compound (6). A careful analysis of the four main peaks observed in the F.T. has been used to estimate the percentage of nickel in the used compounds. Each peak has been filtered, back-Fourier transformed and fitted using experimental phase shifts and amplitudes of the standard Ni foil (figure 3). The mean free path and the edge energy were kept equal to the nickel one; Debye Waller factor varied from 0.02 to 0.04 Å; the calculated distances were those of FCC nickel. For each shell the ratio $N_j/N_j(\text{Ni})$ (N_j = coordination number of the j^{th} shell) was calculated and the percentage of Ni metal was estimated from the mean ratio of the three last shells. As the precision on coordination numbers is quite low in EXAFS, this calculation cannot be used as an absolute value, but it is a good tool to compare the catalysts (table 1).

After catalytic reaction CeNi₂ and CeNi₅ exhibit the same Ce L_{III} edge spectra than CeO₂. It's not the case of CeNiAl or its hydride as seen on figure 4. Spectra were fitted as described in (7). We found that they are a mixing of trivalent Ce oxide (white line with a 5 eV band-width) and CeO₂ (about 20%). This result was confirmed by the M_{IV} - M_V Ce edges, where the mixing of trivalent cerium and CeO₂ clearly appear (figure 5). No conclusion can be brought by La L_{III} edge since no clear difference appears between intermetallics and lanthanum oxides.

Discussion

From the results summarized in table 1 a relation can be established between activation temperature and compounds transformation.

CeNi_x compounds are active at 300°C and they are also the most decomposed into nickel and rare-earth oxide after only 30 hours of reaction. For LaNi_x systems a higher activation temperature (350°C) is necessary. Moreover they are not fully transformed into nickel (EXAFS) and lanthanum oxide is not visible (X.R.D.) except for LaNi₂ which is fully transformed into Ni and La₂O₂CO₃ (XRD) and is also the most active. In the case of CeNiAl compounds the thermal stability is increased up to 400°C by the presence of Al which lead to a trivalent cerium oxide.

These results show that rare earth oxidation play an important role in the catalysts activation. They confirm that catalytic activity is related to the percentage of free nickel particles which are the active sites in this reaction. Nevertheless no easy conclusion can be drawn for the effect of hydrogen absorption since the difference of activity between intermetallics and hydrides depends of their composition.

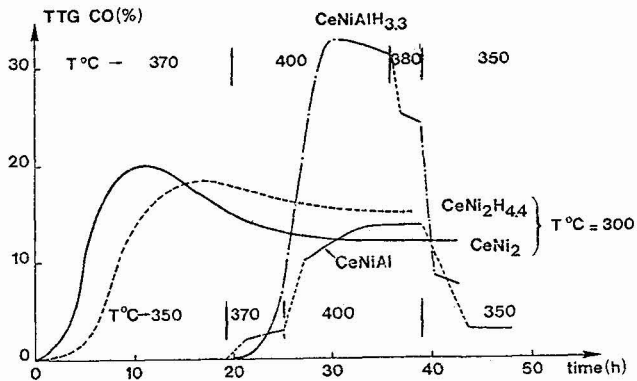


Fig. 1.- Catalytic activity as a function of time and temperature of CeNi₂, CeNiAl and their hydrides.²

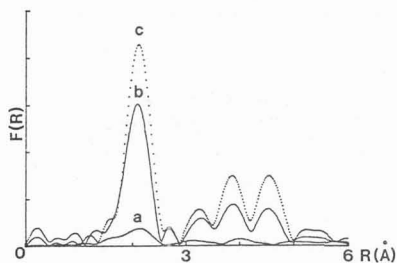


Fig. 2.-F.T. of CeNiAlH₃ before (a) and after (c) catalytic reaction compared to Nickel (b).

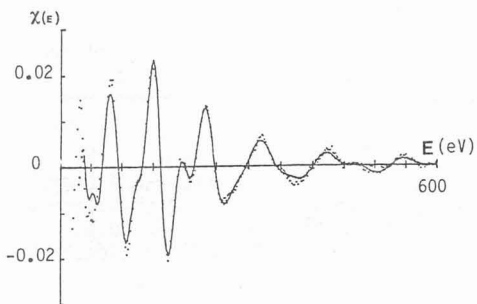


Fig. 3. - EXAFS spectrum of CeNi₂ after reaction:
 experimental
 — simulation with four Ni shells

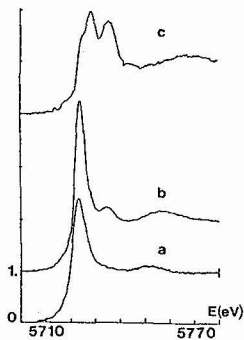


Fig. 6.- Cerium L_{III} edge spectra of CeNiAlH_{3.3} before (a) and after (b) reaction compared to CeO₂

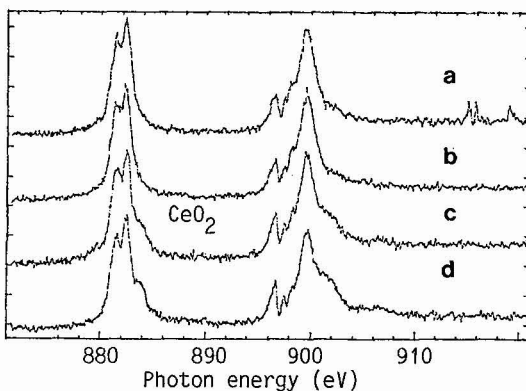


Fig. 5. - Cerium M_{IV-V} edge spectra of CeNiAlH_{3.3} and CeNiAl before (a and b) and after (c and d) catalytic reaction.

Compound	T(°C) (1)	A (2)	t (h) (3)	Phases (XRD)	% Ni (EXAFS)	Ce phases	
						L _{III}	Ni _{IV} -Ni _V
CeNi ₅	300	82	27	Ni+CeO ₂	80	CeO ₂	CeO ₂
CeNi ₂	300	65	30	Ni+CeO ₂	95	CeO ₂	CeO ₂
CeNi ₂ H _{4.4}	300	65	30	Ni ₃ C+CeO ₂			
LaNi ₅	350	38	40	LaNi ₅ +Ni	20		
LaNi ₂	350	104	50	Ni+La ₂ O ₂ CO ₃			
LaNi ₂ H _{4.3}	340	18	53	Ni	40		
CeNiAl	400	18	50	Ni	75	Ce ³⁺ +20%CeO ₂	Ce ³⁺ +yCeO ₂
CeNiAlH _{3.3}	400	48	50	Ni	75	Ce ³⁺ +20%CeO ₂	Ce ³⁺ +yCeO ₂

TABLE 1 - Catalytic properties and characterization results after reaction of RNi_x (R = La, Ce ; x = 2 or 5) and CeNiAl intermetallics and hydrides.
 (1) activation temperature ; (2) activity (mol CO h⁻¹g⁻¹Ni) at 350°C ;
 (3) total time of reaction.

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