

# Synthesis Gas Reactions Using Catalysts Formed by Oxidizing Ni-Containing Intermetallic Compounds

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## I. Introduction

Intermetallic compounds containing rare earths or actinides in chemical union with the transition metals Fe, Co or Ni are transformed when exposed to synthesis gas at elevated temperatures into mixtures of rare earth or actinide oxides and elemental Fe, Co or Ni. It has been found that these mixtures are exceptionally active for syngas conversion (1-12). The converted alloys have been characterized by Auger spectroscopy (1,13), x-ray diffraction, ESCA (14) and electron microscopy (7). These studies showed that the surface regions consisted of transition metal nodules growing out of or dispersed on a substrate of rare earth or actinide oxide. The decomposed materials rather than the original alloy appear to be the catalytically active species for the reaction.

Additionally, it has been found that thorium-containing intermetallics such as ThNi<sub>5</sub> readily reacted with elemental oxygen to form a mixture of metallic Ni and ThO<sub>2</sub> (12). The oxidation of ThNi<sub>5</sub> occurred with a predominant formation of ThO<sub>2</sub> because of the strong chemical affinity of thorium for oxygen. During the oxidation reaction metallic Ni aggregates precipitated out in a fashion similar to that observed when the intermetallic is exposed to syngas. The reaction of ThNi<sub>5</sub> with a stoichiometric amount of oxygen required for the formation of thorium-supported Ni catalysts (Ni/ThO<sub>2</sub>) brought about complete transformation into a mixture of Ni and ThO<sub>2</sub>. This mixture had higher activity for methane formation by an order of magnitude than oxide-supported catalysts (15) prepared by conventional wet chemical procedures. Accordingly, it appears that the oxidation treatment of intermetallics constitutes a novel way for forming oxide-supported catalysts with high activity for syngas conversion.

In this work, the character of catalysts formed by the oxidation of several rare earth-nickel intermetallic compounds was studied in the manner used earlier to study the Th intermetallics. They were evaluated using x-ray diffraction, ESCA and CO chemisorption techniques. The resulting materials, which are probably new supported catalysts, were examined as syngas conversion catalysts.

## II. Experimental

The intermetallic compounds (LaNi<sub>5</sub>, CeNi<sub>5</sub>, PrNi<sub>5</sub>, NdNi<sub>5</sub>, HoNi<sub>5</sub>, ErNi<sub>5</sub> and ThNi<sub>5</sub>) were prepared by induction melting the metal components in a water-cooled copper boat under an atmosphere of purified helium. These intermetallics were subjected to remelting several times or annealing at a prescribed temperature to insure homogeneity. The formation of the desired compounds was established by x-ray diffraction analysis.

The oxidation treatment of the intermetallics, which had been previously powdered in a porcelain mortar followed by outgassing, was conducted in the presence of oxygen at 610 mmHg. The amount of oxygen uptake by the compound was determined by the pressure drop in a closed system.

To establish the nature of the sample thus treated x-ray diffraction, x-ray photoelectron spectroscopy (ESCA) and CO chemisorption techniques were used.

Powder x-ray diffraction patterns were obtained using a Picker model 3488K diffractometer with Cu radiation. ESCA spectra were recorded on an AEI ES200 electron spectrometer using Al K $\alpha$  radiation (1486.6 eV). The spectrometer was operated at 12 KV and 25 mA with base pressure  $<10^{-9}$  torr in the sample chamber. The binding energy was determined by reference to the contamination C 1s line at 285.0 eV. The CO chemisorption measurements were made at room temperature by means of an adsorption flow method (16). The procedures used have been described in detail previously (12).

### III. Results and Discussion

#### 1. Characterization of Catalysts Formed by Oxidation

##### X-RAY DIFFRACTION

The previous work (12) on the oxidation of thorium-containing intermetallic compounds showed that the oxidation reaction occurred in a stepwise fashion. At first, thorium in the alloy was oxidized largely to form the oxide, during which process finely divided Ni aggregates precipitated out on the resulting oxide surface. Accompanying this there was a remarkable enlargement in the surface area, by up to 200-fold. After completion of the oxidation of thorium further oxygen was taken up by the reaction of Ni to form NiO.

All the compounds studied in the present work readily reacted with considerable amounts of oxygen at 350°C. It was confirmed from x-ray diffraction studies that the oxidation steps approximated that of the thorium intermetallics just mentioned. For example, as depicted in Fig. 1, CeNi<sub>5</sub> was completely transformed into a mixture of Ni phase and CeO<sub>2</sub>, i.e., Ni/CeO<sub>2</sub>, when reacted with the stoichiometric amount of oxygen required to oxidize the Ce present in the alloy. When the CeO<sub>2</sub>-Ni mixture was exposed to oxygen there was an additional uptake of oxygen. This occurred by the oxidation of Ni to form NiO. However, after reduction with hydrogen there was no evidence of NiO peaks in the pattern.

From x-ray line broadening measurements of the Ni (111) peak at  $2\theta = 44.5$  (Cu K $\alpha$  radiation) it was possible to establish the Ni particle sizes dispersed on the resulting oxide using the Sherrer equation (18). As shown in Table 1, the particle sizes ranged from 90 to 350 Å. The particle sizes usually but not always showed an increase with increasing oxygen uptake for LaNi<sub>5</sub>, CeNi<sub>5</sub> and ThNi<sub>5</sub>.

##### ESCA

X-ray diffraction studies in the preceding section provided an overall image of the alloy transformed by the oxidation. ESCA measurements were made on the oxidized CeNi<sub>5</sub> to examine the chemical state of the surface species participating in the reaction. ESCA spectra of the oxidized CeNi<sub>5</sub> showed Ni, Ce, O and C signals within the probing depth of ESCA (several atomic layers). Confirming the results obtained by x-ray diffraction analysis, the Ce present in the surface region was found to exist largely in an oxide form. For Ni species the oxidized CeNi<sub>5</sub> (C-4) exhibited the Ni 2p<sub>3/2</sub> peaks at 853.9 and 856.6 eV. These binding energies are characteristic of Ni and NiO, respectively (19). Hence Ni is present in the surface region, consisting of several atomic layers, as metal and oxide. Since the ESCA peak intensity is directly correlated with the surface concentration, the composition of the surface can be roughly established from the ESCA information. The intensity ratio of Ni 2p<sub>3/2</sub> to Ce 3d<sub>5/2</sub>,  $\sim 7.5$ , indicates that the surface is largely metallic Ni.

Table 1. Characterization of Catalysts Formed by Oxidation

Precursor Intermetallic Compound	O <sub>2</sub> Uptake (mmol/g)	Surface Area <sup>a)</sup> (m <sup>2</sup> /g)	CO Chemisorption (μmol/g)	Particle Size (Å)
LaNi <sub>5</sub>	-	0.10*	0.17*	
" (L-1)	1.71	0.55	1.2	90
" (L-2)	2.99	0.66	2.6	100
" (L-3)	6.57	3.5	7.1	100
CeNi <sub>5</sub>	-	0.08*	0.13*	
" (C-1)	2.32	1.1	4.8	110
" (C-2)	3.74	15.7	31.7	300
" (C-3)	4.47	25.4	45.7	200
" (C-4)	5.14	23.7	51.8	350
PrNi <sub>5</sub>	-	0.15*	0.10*	
" (P-1)	1.73	0.79	2.8	170
NdNi <sub>5</sub> (N-1)	1.71	1.1	1.2	140
HoNi <sub>5</sub> (H-1)	1.64	0.76	2.0	330
ErNi <sub>5</sub> (E-1)	1.61	1.0	2.0	280
ThNi <sub>5</sub>	-	0.09*	0.2*	
" (T-1)	1.91	12.0	19.0	200
" (T-2)	3.35	18.0	105.7	270

a) Surface areas were measured at liquid nitrogen temperature by means of argon adsorption (17).

\* These values were obtained for the original intermetallic compounds.

#### CO CHEMISORPTION

Although ESCA studies revealed existence of metallic Ni in the surface region, to obtain the information about the amount of metallic surface area or the number of active sites present on the surface room temperature CO chemisorption measurements were made. The results obtained are summarized in Table 1. It is informative to notice that the oxidized samples (L-1, C-1, P-1, N-1, H-1, E-1 and T-1) contain elemental oxygen corresponding to the complete formation of Ni/oxide assuming a stoichiometric reaction. It is evident that the oxidation led to an increase in the number of active sites along with a rise in the surface area. The extent of the increase was observed to be dependent upon the particular rare earth or actinide involved in the original compound. CeNi<sub>5</sub> and ThNi<sub>5</sub> exhibited striking changes in chemisorption during the stages of oxidation. CO chemisorption increases by up to 500-fold compared to the original compound were observed. In contrast, increases for LaNi<sub>5</sub> were much less pronounced. The differing behavior of CeNi<sub>5</sub> and ThNi<sub>5</sub> on the one hand and LaNi<sub>5</sub> on the other undoubtedly reflects important physicochemical differences. The most significant difference between LaNi<sub>5</sub> and the other two compounds is that La is trivalent and Ce and Th are quadrivalent. This leads to a different electron concentration and perhaps a difference in chemical stability. This may be responsible for variation in

behavior of the systems produced by oxidation, but the precise factors and their operation are as yet unclear.

## 2. Reaction of CO and H<sub>2</sub>

The reaction was carried out in the range of 150 to 300°C over the alloys, which had been oxidized to varying extents. The data obtained are summarized in Table 2. Activity for the present reaction was represented by the rate of CO

Table 2. Activity of Various Catalysts

Precursor Intermetallic Compound	CO Conversion (%)	Activity (ml/sec.g)	T.N.x10 <sup>3</sup> (sec <sup>-1</sup> )
LaNi <sub>5</sub> (L-1)	1.2	1.5x10 <sup>-3</sup>	48
CeNi <sub>5</sub> (C-1)	2.0	2.5x10 <sup>-3</sup>	18
" (C-2)	1.0*	1.2x10 <sup>-3*</sup>	
" (C-3)	2.6*	3.7x10 <sup>-3*</sup>	1.7*
" (C-4)	5.0*	6.1x10 <sup>-3*</sup>	3.8*
PrNi <sub>5</sub> (P-1)	1.8	2.2x10 <sup>-3</sup>	26
NdNi <sub>5</sub> (N-1)	0.5	6.1x10 <sup>-4</sup>	19
HoNi <sub>5</sub> (H-1)	1.6	2.0x10 <sup>-3</sup>	31
ErNi <sub>5</sub> (E-1)	4.2	5.2x10 <sup>-3</sup>	59
ThNi <sub>5</sub> (T-1)	9.0*	1.1x10 <sup>-2*</sup>	10.6*
" (T-2)	7.0(at 190°C)	3.5x10 <sup>-2*</sup>	5.6*

\* The values correspond to the results measured at 205°C; the others were obtained at 275°C, except as noted.

consumption per gram-catalyst. This kind of comparison seems valid since the catalysts were used under very similar conditions. Taking into account the fact that the catalytically active species is metallic Ni dispersed on the surface, it is also of interest to specify the turnover number (T.N.), representing the specific activity per site. The turnover number as molecules CH<sub>4</sub> produced per site per second was determined from CO chemisorption measurements assuming a 1:1 ratio of a CO molecule to surface Ni atom in the surface complex. Among the catalysts studied the oxidized CeNi<sub>5</sub> and ThNi<sub>5</sub> exhibited exceptional activity (Table 2). The oxidized CeNi<sub>5</sub> and ThNi<sub>5</sub> showed T.N. measured at 205°C about an order of magnitude higher than conventional silica- or alumina-supported Ni catalysts (15). It is therefore apparent that the supported catalysts derived using the oxidation treatment of intermetallics are exceptionally active for the conversion of CO and H<sub>2</sub> to methane. T. Inui et al. (20) have reported that activity for methanation was substantially enhanced when ~3% rare earth oxide such as La<sub>2</sub>O<sub>3</sub> or Ce<sub>2</sub>O<sub>3</sub> was added to Ni-supported catalysts. It was found (21) that ThO<sub>2</sub> was also operative as a promoter for supported Ni catalysts.

It should be emphasized that the effectiveness of rare earth or actinide oxide-supported catalysts for syngas conversion is very dependent upon the preparation method. As noted in the Introduction, for example, a ThO<sub>2</sub>-supported catalyst (6) prepared using the conventional impregnation procedure followed by calcining and reducing processes exhibited very poor activity compared to that obtained by the oxidation technique. It thus appears that the oxidation treatment of intermetallics plays a decisive role in formation of active catalysts and this method constitutes a new way of producing superior oxide-supported catalysts.

As shown in Table 2, for the oxidized CeNi<sub>5</sub> and ThNi<sub>5</sub> increase in the extent of oxidation results in an increase in the activity. There is a good correspondence between the CO chemisorption and activity and in this respect the present systems closely resemble behavior observed earlier for oxidized Ni<sub>5</sub>Si<sub>2</sub> (22).

Hydrocarbon products in the reaction were largely methane. Small amounts of C<sub>2</sub> to C<sub>4</sub> hydrocarbons were also observed. Selectivity of hydrocarbon products over various oxidized alloys is listed in Table 3. The selectivity was determined in

Table 3. Selectivity of Catalysts

Precursor Intermetallic Compound	Conversion (%)	Composition (%)			
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
LaNi <sub>5</sub> (L-1)	1.8	92.0	7.0	1.0	-
CeNi <sub>5</sub> (C-1)	3.4	86.3	7.0	5.3	-
" (C-4)	5.0	77.3	15.9	6.8	-
PrNi <sub>5</sub> (P-1)	3.1	88.4	6.6	5.0	-
NdNi <sub>5</sub> (N-1)	1.8	91.3	4.3	4.3	-
HoNi <sub>5</sub> (H-1)	2.5	82.4	8.1	9.5	-
ErNi <sub>5</sub> (E-1)	4.2	74.0	10.9	15.0	-
ThNi <sub>5</sub> (T-1)	12.5	80.0	12.1	6.8	1.4

the conversion range below 10%. It is unclear from this study whether the selectivity is dependent upon extent of the total conversion. It is to be noted that the selectivity depends upon the nature of the rare earth or actinide in the precursor compound. Oxidized LaNi<sub>5</sub> revealed very high selectivity for methane formation. This accords with the observation of T. Inui et al. (20) referred to above.

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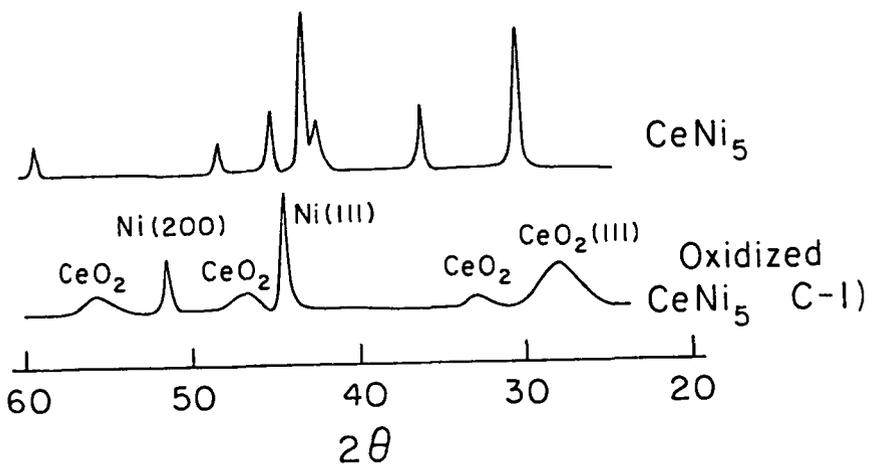


Fig. 1 Comparison of x-ray diffraction (Cu  $K\alpha$  radiation) of the oxidized and original  $CeNi_5$ .