JOURNAL OF CATALYSIS 65, 127–132 (1980)

Synthesis Gas Reactions over Catalysts Formed by Oxidation of Thorium-Containing Intermetallic Compounds

H. IMAMURA AND W. E. WALLACE

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received September 12, 1979; revised February 29, 1980

The intermetallic compounds (ThNi, $ThNi_2$, $ThNi_5$, and Th_7Ni_3) react readily with oxygen to form an intimate mixture of Ni and ThO_2. These mixtures have been characterized by X-ray diffraction and CO and H_2 chemisorption measurements. The CO chemisorption increased markedly during the oxidation process. Increases by up to 500-fold compared to the original compound were observed. The Ni–ThO_2 mixtures showed high activity for catalyzing the production of CH_4 from synthesis gas. Hence, the oxidation process can be considered to be a new way of producing oxide-supported Ni catalysts. Turnover numbers for the new catalysts at 205°C were found to be much larger than those of conventional oxide-supported catalysts.

I. INTRODUCTION

Recently, a wide variety of intermetallic compounds consisting of rare earth or actinide metals combined with the transition metals (Fe, Co, and Ni) have been found to be catalytically active in the formation of methane from synthesis gas ($H_2/CO = 3$) (*1–11*). It was found that among the compounds studied to date, $ThNi_5$ (*2, 7*) was particularly active; its specific activity, turnover number, was found to be considerably higher than that of supported nickel catalysts formed by conventional wet chemical means (*12, 13*). The work on $ThNi_5$ showed that during the reaction $ThNi_5$ was extensively decomposed into Ni and ThO_2. Using the scanning electron microscope it was established that the surface consisted of Ni nodules growing out of or supported on ThO_2 (*3*). These decomposition products rather than the original intermetallic compound appear to be the actual catalyst.

More recently, it has been observed (*14, 15*) that some intermetallic compounds (Ni_5Si_2, Ni_2Si, and Co_2Si) readily react with elemental oxygen to form mixtures containing Ni or Co and SiO_2, and these mixtures are also quite active as methanation catalysts. These exhibited considerably higher activity as methanation catalysts than conventionally formed silica-supported catalysts. The earlier work shows that the oxidation of alloys constitutes a new way of forming supported catalysts. This novel class of supported catalysts is of great interest because of their exceptional activity.

The present study was undertaken to investigate the oxidation treatment of $ThNi_5$, which, as indicated above, decomposes when exposed to synthesis gas to form a very active catalyst and some homologous compounds (ThNi, $ThNi_2$, and Th_7Ni_3), and to determine the activity of the oxidized alloys for the methanation reaction.

II. EXPERIMENTAL

The intermetallic compounds (ThNi, $ThNi_2$, $ThNi_5$, and Th_7Ni_3) were prepared by induction melting the metal components in a water-cooled copper boat under a purified argon atmosphere. These compounds were remelted several times to ensure homogeneity. The desired structure of the intermetallics was verified by X-ray diffraction analysis.

0021-9517/80/090127-06$02.00/0

Oxidation treatment of the samples, which had been previously powdered in air by a mortar and pestle followed by outgassing at 300°C, was carried out by introducing oxygen at 610 mm Hg in a closed system (~200 ml). Oxygen uptake by the alloys studied was determined by the pressure drop in a closed system.

To obtain information about the metallic surface area, CO and H_2 chemisorption measurements were made at room temperature by means of the adsorption flow method of Gruber (*16*). This technique consists of injecting a known amount of CO (or H_2) in front of the catalyst bed into a helium stream and detecting, by a thermal conductivity method, the amount of CO (or H_2) not taken up by the catalyst. Accuracy of this method was experimentally confirmed within an error of a few percent from comparison with the results which were obtained using the conventional BET method for the same sample. Prior to every chemisorption measurement the oxidized samples were heated at 350°C under vacuum (~10^{-5} Torr), reduced at 400°C for 2 hr in a purified hydrogen flow at 1 atm (30 ml/min), and then evacuated at the same temperature for 1 hr.

The reaction of CO with H_2 was studied in a single-pass microreactor operating at 1 atm total pressure. From each sample thus treated, 0.5 g was supported on glass wool in the reactor and subjected to the following treatments before each measurement. The catalysts were outgassed at 350°C for 3 hr, reduced at 400°C in a purified hydrogen flow at 1 atm (30 ml/min), and then gradually cooled to room temperature. After the reactor containing the catalysts was briefly evacuated to remove hydrogen in the gas phase, synthesis gas purified by passage through a molecular sieve and a liquid nitrogen trap was admitted into the system at a flow rate of 15 ml/min. A portion of the reacting gas was drawn from the system into a gas sampler and transferred to a gas chromatograph with a 0.25-in. × 10-ft Porapax Q column.

III. RESULTS AND DISCUSSION

A. *Formation and Characterization of Catalysts Produced by Oxidation*

Oxygen uptake by the alloys studied was determined by the method indicated in the previous section. A typical time course of the oxygen uptake at 350°C by $ThNi_5$ is depicted in Fig. 1. The reaction proceeded through a rapid initial stage lasting about 2 hr, followed by a slower stage of oxidation. To ascertain the nature of the systems formed during the oxidation treatment a series of powder X-ray diffraction studies were made. Representative X-ray diffraction patterns of $ThNi_5$ reacting with various amounts of oxygen are illustrated in Fig. 2 together with that of the unoxidized sample. Peaks at 44.5 and 51.8° and at 27.6 and 54.3° 2θ (Cu$K\alpha$ radiation) in the diffraction patterns can be assigned to Ni metal (111, 200) and thorium dioxide (ThO_2) (111, 311), respectively. As the oxidation reaction progressed, the original peaks of $ThNi_5$ gradually disappeared and intensities of the peaks corresponding to metallic Ni and ThO_2 increased markedly. For the oxidized $ThNi_5$, designated T-4, which reacted with oxygen corresponding to the amount required for the compete conversion into Ni and ThO_2 (i.e., Ni/ThO_2), the diffraction patterns showed only the existence of metallic Ni and ThO_2. The oxidized $ThNi_5$ (T–

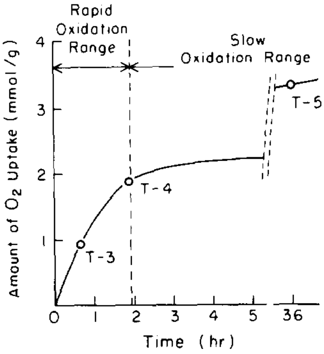

FIG. 1. Time course of oxygen uptake by $ThNi_5$ at 350°C. The oxidation reaction was conducted at 350°C over $ThNi_5$ in the presence of O_2 at 610 mm Hg.

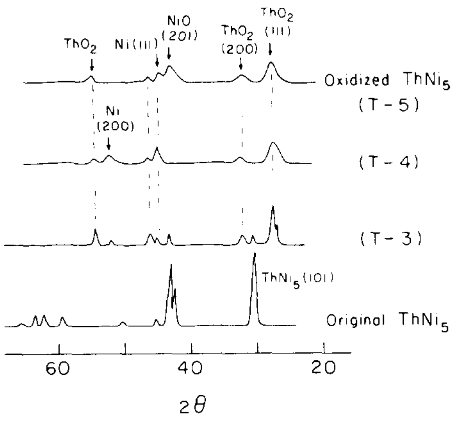

FIG. 2. X-Ray diffraction patterns of oxidized $ThNi_5$ (T-3, T-4, T-5) and original $ThNi_5$. X-Ray diffraction measurement was made by the powder method.

3), containing oxygen corresponding to 41% transformation of the catalyst for the completeness, still possessed a slight amount of the original material along with metallic Ni and ThO_2. These observations strongly suggest that in the rapid-oxidation stage the degree of the oxidation determines the extent of transformation of $ThNi_5$ into Ni/ThO_2. Further oxidation, in the range of the slow process (Fig. 1), results in formation of NiO, which is indicated by the peak at 43.4° in the diffraction pattern (Fig. 2). However, there was no observation of NiO after reduction of the catalyst. In brief, the reaction of $ThNi_5$ with oxygen can be considered to progress stepwise as follows: At first, oxygen taken up by $ThNi_5$ selectively reacts with thorium to form thorium dioxide with great rapidity, because of a strong affinity of thorium for oxygen (standard free energy of formation is ~250 kcal/mol) and Ni aggregates precipitate out to form Ni deposited on a ThO_2 support (The metallic Ni phase produced in this way was found to be finely dispersed with the particle sizes in the range of 180 to 270 Å as determined from X-ray line-broadening measurements (*17*) of the Ni peak at $2\theta = 44.5°$.) Then, Ni dispersed on ThO_2 is gradually oxidized to produce nickel oxide. Th_7Ni_3 readily reacted with oxygen at 350°C in a manner similar to that of $ThNi_5$. ThNi and $ThNi_2$ reacted with oxygen at room temperature without difficulty. This striking difference in the reactivity of the alloys for oxygen may be attributed to differences in crystal structure. $ThNi_2$, $ThNi_5$, and Th_7Ni_3 are hexagonal whereas ThNi is orthorhombic. In addition, the reactivity appears to be extensively enhanced with an increase in the Th:Ni ratio in the intermetallic compound.

The catalysts thus prepared by the oxidation treatment were characterized by CO chemisorption to provide information about the metallic surface area. Data obtained are summarized in Table 1. Attempts were made to perform H_2 chemisorption measurements as well. These gave unrealistically large apparent absorption, perhaps because of the absorption of hydrogen into the underlying intermetallic layer. Systems such as these are well-known hydrogen absorbers (*18*). The oxidized $ThNi_5$ (T-4), for example, took up 121.4 μmol H_2 per gram. This is larger by a factor of about 6 than the CO chemisorption result. Other Th–Ni systems exhibited a similar behavior.

There appears to be a strong interaction between hydrogen and $ThNi_5$. One indication of this is the large chemisorption described in the preceding paragraph. ESCA measurements on $ThNi_5$ show (*19*) that treatment with hydrogen produces a substantial surface enrichment of Ni. Evidently hydrogen draws Ni to the surface. These features may be closely related to the exceptionally high activity of the oxidized materials as methanation catalysts, as described below in Section B.

As shown in Table 1, the oxidation treatment, in all cases, led to a considerable increase in CO chemisorption. For oxidized $ThNi_5$, CO chemisorption increased strikingly with the extent of the oxidation. It is not entirely clear why the amount of CO chemisorption increased in the range of the

TABLE 1

Characterization of Catalysts Formed by Oxidation

Catalyst	Oxidation temperature (°C)	O_2 uptake (mmol/g)	Surface area (m^2/g)	CO chemisorption (μmol/g)
ThNi	—	—	0.10[a]	0.15[a]
ThNi (T-1)[b]	r.t.	3.38	16.0	37.6
$ThNi_2$	—	—	0.08[a]	0.13[a]
$ThNi_2$ (T-2)[b]	r.t.	2.82	14.3	34.7
$ThNi_5$	—	—	0.09[a]	0.2[a]
$ThNi_5$ (T-3)	350	0.94	3.93	6.5
$ThNi_5$ (T-4)[b]	350	1.91	12.0	19.0
$ThNi_5$ (T-5)	350	3.35	18.8	105.7
Th_7Ni_3	—	—	0.08[a]	0.17[a]
Th_7Ni_3 (T-6)[b]	350	3.84	8.4	33.0
3.9%-Ni/ThO_2[c]	—	—	6.1	17.0(3.9)[d]

[a] These values correspond to the results obtained for the original alloys.

[b] These catalysts contain oxygen corresponding to complete transformation into Ni/ThO_2.

[c] The catalyst was prepared by the conventional impregnation method as described in the text.

[d] The value in parentheses is the value obtained by H_2 chemisorption.

slow-oxidation process (T–4 → T–5: Fig. 1) which, from X-ray diffraction analysis, appears to have been due to the formation of NiO from Ni. This may be due to an increase in degree of metal dispersion on ThO_2 as a carrier during the course of the oxidation.

The degree of Ni dispersion for the oxidized alloys is shown in Table 2. The degree of dispersion was calculated according to the equation

$$\text{Degree of dispersion} = \frac{C}{W} \times 100,$$

where C and W denote the CO chemisorption and content of Ni per unit weight of catalyst, respectively. It is assumed in this calculation that a CO molecule interacts with a Ni metal atom to form a surface complex of 1 : 1 ratio.

TABLE 2

Degree of Dispersion for Catalysts Formed by Oxidation

Catalyst	Degree of dispersion (%)
ThNi (T-1)	1.2
$ThNi_2$ (T-2)	1.3
$ThNi_5$ (T-4)	1.1
$ThNi_5$ (T-5)	5.9
Th_7Ni_3 (T-6)	6.0

Note that surface areas measured at liquid nitrogen temperature by means of argon adsorption (*20*) showed a very striking increase, to a maximum of about 200-fold, during the oxidation reaction.

B. Methanation Reaction over Catalysts Formed by Oxidation

The reaction was conducted over the oxidized alloys (ThNi, $ThNi_2$, $ThNi_5$, and Th_7Ni_3) by admitting the synthesis gas (H_2/CO = 3). The reaction temperature ranged from 150 to 220°C to maintain the total conversion below 10%, so as to minimize heat and mass transport problems. The results obtained are summarized in Table 3. Activity of the catalysts studied were determined from the rate of CO consumption per gram of catalyst under steady-state conditions. Turnover numbers (N) as molecules CH_4 formed per site per second were also determined (Table 3) assuming equivalence between the number of active sites and the number of CO molecules chemisorbed.

TABLE 3

Activity of Various Catalysts

Catalyst	CO conversion at 205°C (%)	Activity at 205°C (ml/g-sec)	Activation energy (kcal/mol)	$N \times 10^3$ at 205°C (sec^{-1})
ThNi (T-1)	4.0	4.9×10^{-3}		2.7
$ThNi_2$ (T-2)	3.2	4.0×10^{-3}		2.9
$ThNi_5$ (T-3)	1.5	1.9×10^{-3}		8.7
$ThNi_5$ (T-4)	9.0	1.1×10^{-2}		10.6
$ThNi_5$ (T-5)	7.0 (at 190°C)	3.5×10^{-2a}	27.2	5.6[a]
Th_7Ni_3 (T-6)	2.6	3.2×10^{-3}		2.8
$ThNi_5$				4.7[b]
25% Ni/ThO_2[c]	1.7 (at 510°C)			
3.9% Ni/ThO_2[c]	2.0 (at 490°C)	2.9×10^{-3} (at 490°C)		

[a] The values at 205°C were obtained by extrapolation to 205°C from the Arrhenius plots.

[b] Results obtained when $ThNi_5$ is transformed by reaction with synthesis gas.

[c] The catalysts were prepared by conventional impregnation techniques as described in the text.

Reaction products were predominently CH_4, CO_2, and H_2O; trace amounts of higher hydrocarbons (C_2, C_3, and C_4) were observed. High selectivity for methane was observed in all cases. Turnover numbers measured at 205°C for the oxidized $ThNi_5$ were considerably higher than those of conventional alumina- or silica-supported Ni catalysts (*12*). The oxidized Th–Ni systems have turnover numbers comparable to Ni/TiO_2 catalysts for which superior deactivation resistance has been recently announced (*13*). The exceptional activity of the catalysts formed by the oxidation treatment is evident. For the oxidized $ThNi_5$, as shown in Fig. 3, the activity for the reaction was found to increase considerably with increasing oxygen uptake. This result correlated well with the CO chemisorption results (see Table 1). This behavior closely resembles that of the oxidized Ni_5Si_2 studied earlier (*15*).

ThO_2 has been recognized as an effective additive for Ni catalysts, significantly improving activity and selectivity (*21*). It was reported that increasing ThO_2 content tended to increase the formation of higher hydrocarbons. Although production of higher hydrocarbons was observed in the high CO conversion in the elevated temperature range in this study, hydrocarbon selectivity of the oxidized. $ThNi_5$ (T–4) around 200°C was as follows: C_1: 80.0%, C_2: 11.8%, C_3: 6.8%, C_4: 1.4%.

As noted in earlier studies from this laboratory (*2*, *7*), $ThNi_5$ was extensively transformed when exposed to a mixture of CO and H_2 ($H_2/CO = 3$) at ~300°C. This transformation was qualitatively established by X-ray diffraction analysis, electron microscopy, and EDAX measurements, which showed the formation of Ni nodules ~0.5 μm in diameter situated on a substrate of ThO_2. It is of interest to compare the activity of the oxidized $ThNi_5$ and the $ThNi_5$ decomposed by exposure to the synthesis gas. The resulting materials in

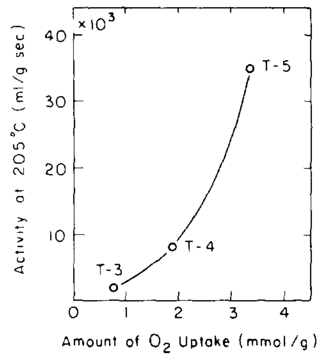

FIG. 3. Effect of oxygen amount in catalysts on activity. The methanation reaction was carried out over $ThNi_5$ containing various amounts of oxygen.

each case had a dark grey color without metallic luster. The data in Table 3 showed that the turnover numbers at 205°C for T–3 and the catalyst formed by reaction with synthesis gas were not very different. Accordingly, it may be concluded that the oxidation treatment and the reaction of alloys with CO and H_2 resulted in essentially the same transformation of the intermetallic compounds. A similar behavior was also observed in the methanation over the oxidized and unoxidized Ni_5Si_2, Ni_2Si, and Co_2Si (*14*).

For a further comparison of activities Table 3 also contains the results (*7*) for thoria-supported catalysts containing 3.9 or 25% Ni, which were prepared by impregnation of thoria with nickel nitrate in an aqueous solution. The materials were dried at 120°C overnight and then reduced in a purified hydrogen flow at 450°C for 2 hr. The catalysts formed by the oxidation exhibited much higher specific activity than the 3.9 or 25% Ni/ThO_2 prepared using the conventional impregnation technique (see Section A).

In conclusion it is evident that the oxidation of alloys provides a new way of producing supported catalysts. These new catalysts exhibit activities for synthesis gas conversion greatly superior to that of the corresponding supported catalysts prepared by conventional wet chemical procedures.

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