

THERMAL STUDIES ON HIGH TEMPERATURE OXIDATION BEHAVIOUR OF NICKEL CONTAINING AB₅ TYPE INTERMETALLICS

J. CHRISTOPHER, M.P. SRIDHAR KUMAR AND C.S. SWAMY

Department of Chemistry, Indian Institute of Technology, Madras 600 036 (India)

(Received 19 June 1989)

ABSTRACT

The oxidation behaviour of nickel containing AB₅ type intermetallic compounds LaNi₅ and CaNi₅ has been studied in an oxygen atmosphere by thermogravimetric (TG) and differential thermal analysis (DTA). The TG of LaNi₅ showed complete oxidation of lanthanum and nickel whereas that of CaNi₅ showed partial oxidation. The DTA curve of LaNi₅ showed four irreversible peaks, which have been attributed to the formation of La₂O₃, NiO and ternary oxides. However, the DTA pattern of CaNi₅ did not show any maxima, indicating slow oxidation of CaNi₅. The difference in the oxidation behaviour has been explained on the basis of the formation of ternary oxides and the heat of reaction.

INTRODUCTION

Nickel-containing hydrogen storage intermetallic compounds like LaNi₅ and CaNi₅ are found to be active catalysts for various important reactions such as CO hydrogenation and other reactions [1–3]. In many instances the specific activities of catalysts derived from these intermetallics are found to be greater (sometimes by about an order of magnitude) than those of the conventionally prepared or even the commercially used catalysts [4]. In all these reactions, it has been observed that the use of oxygen-containing reactants led to the decomposition of the intermetallics into supported metal systems with nickel as the active phase [5,6]. Detailed surface studies [7] on the AB₅ type intermetallics used as catalysts have led to the conclusion that the active phase for the reactions is the B metal supported on the oxide of the A element. These systems have been viewed [8] as a new generation of supported metal catalysts which are active in various hydrogenation/dehydrogenation reactions. Increasing interest is being shown in this new method of preparation of supported metal systems because it helps to solve some important problems associated with conventional catalyst preparation, such as those arising from the use of metal salts (anionic effect) and the impurities that conventional supports often contain [9]. Shiotsuka et al.

[10], in a series of studies, have evaluated the effect of oxidation of these intermetallics on surface area, nickel crystallite size, dispersion of active nickel and their catalytic activity.

In continuation of our previous report on the oxidation behaviour of AB₅ type intermetallic compounds [11], an attempt has been made to follow the oxidation process in more detail with the help of thermogravimetry (TG), differential thermal analysis (DTA) and X-ray diffraction (XRD). More light is thrown on the order of formation of various phases and the temperature of their formation during the oxidation of the intermetallics. Some interesting observations have been made during the thermal analysis of the oxidation of LaNi₅ alloy.

EXPERIMENTAL

The intermetallic compounds CaNi₅ and LaNi₅ employed in this investigation were obtained from Ergenics division of the MPD Technology Corporation, U.S.A., and had the designations HYSTOR 201 and 205 respectively. The phases formed during oxidation of CaNi₅ and LaNi₅ in a flow of oxygen were characterized by X-ray diffractograms obtained with a Philips diffractometer (model PW 1130) provided with an on-line recorder and a dot matrix printer (Teletype, U.S.A). Thermal studies were carried out by TG and DTA techniques using thermal analysis equipment (Perkin-Elmer TGA 7 and Stanton Redcroft, U.K.), and oxidation of CaNi₅ and LaNi₅ was performed at different heating rates with varying amounts of the sample. The flow rate of oxygen was 50 ml min⁻¹.

RESULTS AND DISCUSSION

Thermal studies on LaNi₅

The TG curves recorded at different heating rates for the LaNi₅ sample are shown in Fig. 1. Some interesting observations were made when larger weights (≈ 50 mg) of the alloy powder were employed for TG experiments. Initially there was a gradual increase in weight up to about 5% with heating rates of 10 and 15°C min⁻¹, and then a steep increase in weight was observed at 430°C; thereafter the weight remained almost constant (Fig. 1(a)). The steep increase in weight was preceded by a glow which could be observed from the top of the furnace. When the rate of heating was greater than 15°C min⁻¹, the initial gradual weight increase was not observed, but a sudden increase in weight (along with a glow) was observed at lower temperatures (310 for 18°C min⁻¹). The total increase in weight at 800°C

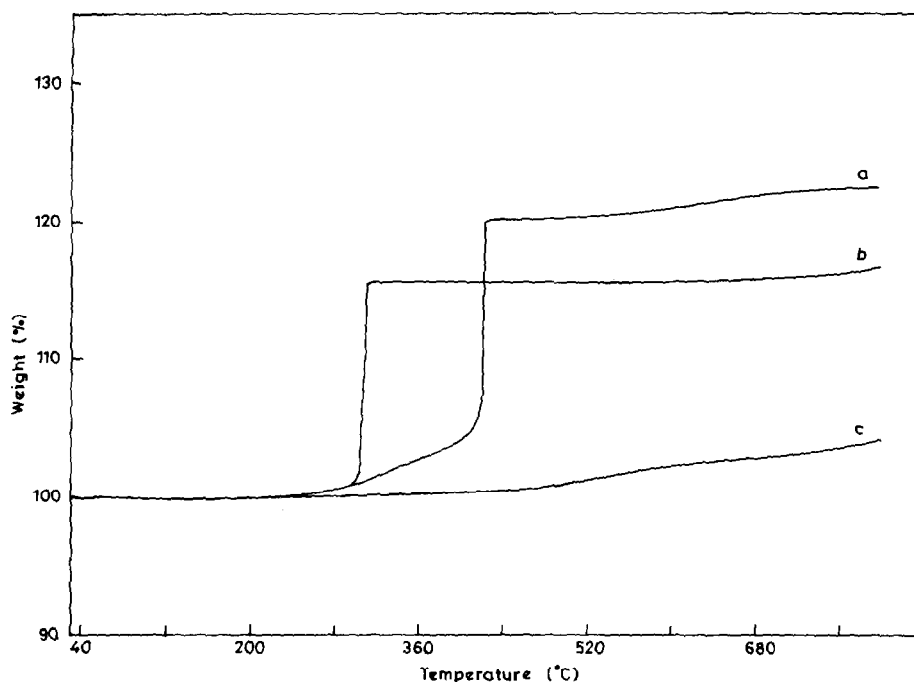


Fig. 1. Thermogravimetric curves of LaNi_5 with heating rates of $10^\circ\text{C min}^{-1}$ (curve a) and $18^\circ\text{C min}^{-1}$ (curve b), and CaNi_5 at $10^\circ\text{C min}^{-1}$ (curve c).

was 16% with heating rates greater than $15^\circ\text{C min}^{-1}$, as compared with 23% observed with heating rates less than $15^\circ\text{C min}^{-1}$.

The glow observed might be a consequence of the highly exothermic reaction due to oxidation of lanthanum and nickel. Because of the large amount of the alloy present and the sudden heating, a steep increase in weight was observed due to the oxidation process. Because of local heating to very high temperatures in such a process, sintered particles of the oxide encapsulating some unreacted alloy particles might be formed. Such an encapsulation of unreacted alloy by CeO_2 has been reported for Ce-Cu intermetallics [12]. This would account for the observation of weight change corresponding to incomplete oxidation (for complete oxidation the weight increase was 24.05%. However, on further heating to higher temperatures in a flow of oxygen, the unreacted portions of the alloy particles slowly begin to be oxidized, resulting in further increases in weight owing to slow diffusion of oxygen into the bulk of the particles.

At lower heating rates ($< 15^\circ\text{C min}^{-1}$), a gradual increase in weight is observed initially, which results from slow oxidation of part of the lanthanum, followed by sudden oxidation of both lanthanum and nickel. Such an initial gradual increase was not observed with higher heating rates, and this might be due to the drastic increase in temperature leading to local heating and simultaneous oxidation of lanthanum and nickel. This local

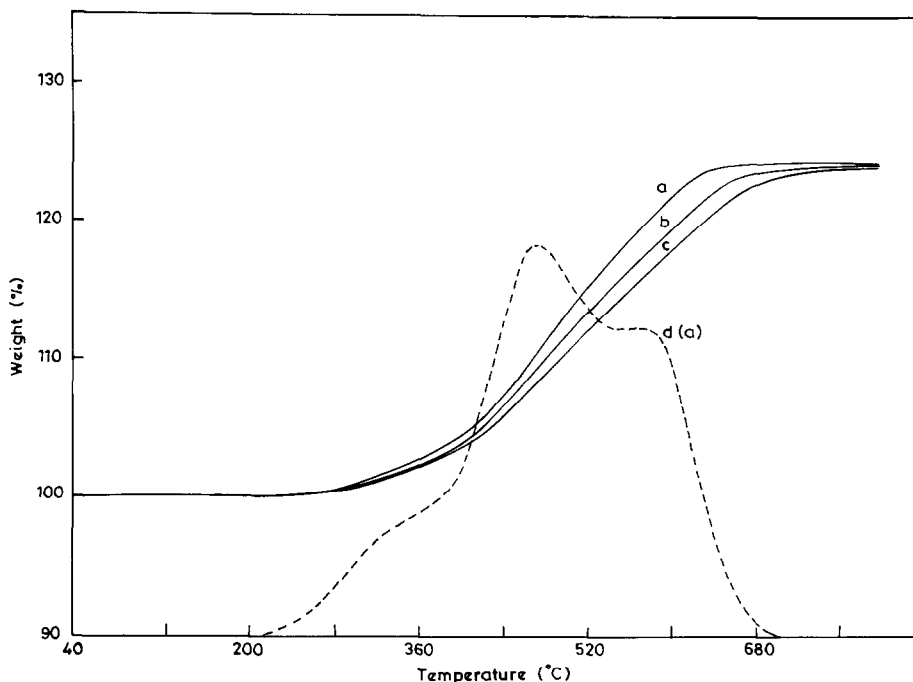


Fig. 2. Thermogravimetric curves of LaNi_5 at different heating rates: curve a, $10^\circ\text{C min}^{-1}$; curve b, $20^\circ\text{C min}^{-1}$; curve c, $30^\circ\text{C min}^{-1}$; and curve d, derivative of TG curve a.

heating also leads to oxidation of nickel at temperatures much lower than those normally observed for the process.

In order to minimize local heating, TG runs have been carried out with smaller amounts of sample ($< 10\text{ mg}$). The TG curves for the oxidation of LaNi_5 in a flow of oxygen at various heating rates are shown in Fig. 2. The weight of the sample reached a constant value at 650°C with a heating rate of $10^\circ\text{C min}^{-1}$, indicating completion of oxidation. The derivative of the TG curve for oxidation of LaNi_5 showed four peaks, indicating four different oxidation processes (Fig. 2d). In order to ascertain the nature of phases formed in such a process, a separate experiment was carried out in a tubular furnace.

A sample of LaNi_5 alloy was heated in a tubular furnace at a heating rate of $10^\circ\text{C min}^{-1}$ up to 650°C , and the phases formed were identified by XRD. The diffractogram did not show the presence of LaNi_5 or Ni. The major phases that could be detected by XRD were NiO, La_2O_3 and LaNiO_3 [11]. The presence of La_2NiO_4 could not be confirmed because of the broadening of the La_2O_3 and LaNiO_3 peaks. Only NiO showed a sharp peak indicating crystallinity. Thus, it is clear from this study that LaNi_5 is completely oxidized to La_2O_3 and NiO along with the formation of ternary oxides. Formation of such a ternary phase has been reported for the system SmCo_5 [13]. As can be seen from Table 1, the observed weight increase is

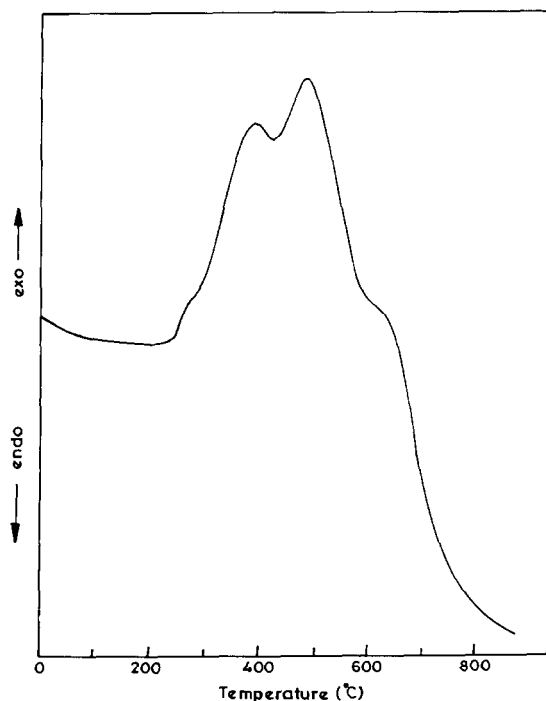
TABLE 1

Results of TG-DTA studies on LaNi_5 (weight < 10 mg)

Heating rate ($^{\circ}\text{C min}^{-1}$)	DTA peak positions ($^{\circ}\text{C}$)				Weight increase up to 900 $^{\circ}\text{C}$ (%)
	1	2	3	4	
10	252.6	369.8	460.7	563.0	24.83
20	268.4	384.5	470.5	609.1	25.17
30	294.5	394.3	493.6	641.3	25.13

greater than that corresponding to the reaction $\text{LaNi}_5 \rightarrow 1/2\text{La}_2\text{O}_3 + 5\text{NiO}$, indicating the formation of ternary oxides, which requires excess oxygen.

The DTA pattern for the oxidation of LaNi_5 in a flow of oxygen showed four exothermic peaks at each heating rate (Table 1). Representative DTA peaks observed at $20^{\circ}\text{C min}^{-1}$ are shown in Fig. 3. The four exothermic peaks at various heating rates are found to have similar shape and intensity to those from DTG (Fig. 2d). In order to verify if any of the DTA peaks were due to a phase transition resulting from the temperature increase, the sample after heating to 900°C at $20^{\circ}\text{C min}^{-1}$ was cooled at the same rate and the DTA pattern was recorded. It was observed in the cooling run that no peaks were apparent and the weight of the sample remained constant,

Fig. 3. DTA pattern of LaNi_5 at $20^{\circ}\text{C min}^{-1}$.

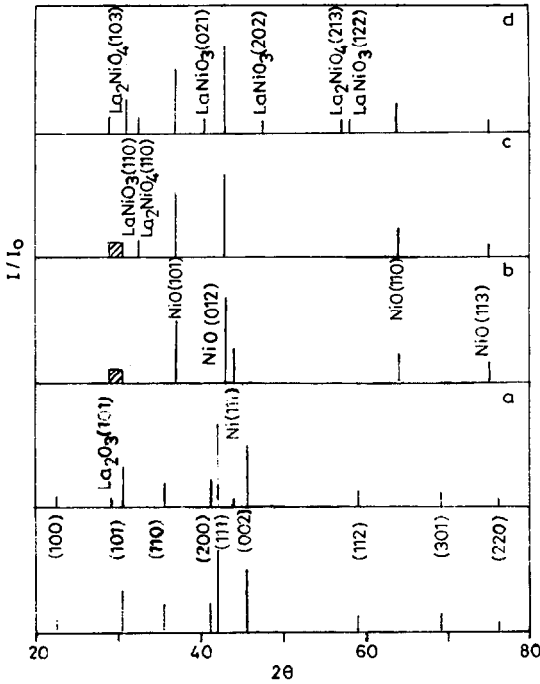


Fig. 4. XRD pattern of LaNi_5 oxidized at different temperatures for 8 h: a, 255 °C; b, 370 °C; c, 460 °C; and d, 560 °C.

thereby ruling out the possibility of a phase transition in the temperature range studied. This also indicates that all the DTA peaks arise due to irreversible transformations under reaction conditions.

In order to assign the four exothermic peaks in DTA to the different irreversible processes occurring during the course of the experiment, and to have a better understanding of the oxidation process, a series of experiments was carried out isothermally, heating the LaNi_5 sample in a flow of oxygen for a period of 2 h at temperatures corresponding to each of the DTA peak

TABLE 2

Isothermal study on LaNi_5 by TG-DTA (weight < 10 mg; duration 2 h)

Temperature (°C)	Weight increase after 2 h (%)	XRD (phases)
255	5	LaNi_5 , Ni ^a , La_2O_3 ^a
370	11.7	NiO, La_2O_3 , Ni ^a
460	23.5	NiO, La_2O_3 ^a , LaNiO_3 ^a , La_2NiO_4 ^a
560	25.8	NiO, La_2O_3 ^a , LaNiO_3 ^a , La_2NiO_4 ^a

^a Trace amounts.

temperatures. The samples (< 10 mg) were heated at a rate of $10^{\circ}\text{C min}^{-1}$ up to the isothermal temperature. Changes in weight of the sample at the end of the experiments were recorded. Simultaneously, a separate set of experiments was carried out in a tubular furnace in an oxygen flow for 8 h at these four temperatures, and the phases formed were characterized by XRD. The XRD patterns are compiled in Fig. 4 along with the pattern of the alloy. The TG and XRD results for these experimental runs are summarized in Table 2. The samples treated at 255, 370, 460 and 560°C were labelled as A, B, C and D respectively. In the DTA runs, at the end of the 2 h period, only in the case of sample D was attainment of constant weight observed; with all the other samples there was a continuous increase in weight, indicating incomplete reaction due to insufficient time being allowed.

Sample A showed a 5% increase in weight, and the XRD pattern of the sample indicated a partial disproportionation of the intermetallic compound resulting from the oxidation of lanthanum to La_2O_3 with the separation of Ni (Fig. 4a). Thus, the peak at 255°C can be assigned to the exothermic oxidation of lanthanum to La_2O_3 . This confirms our results reported earlier [11]. XRD of sample B showed the complete disappearance of the alloy; a considerable amount of nickel was oxidized to NiO, leaving only a small part of it in the metallic form and the lanthanum was completely oxidized to La_2O_3 (Fig. 4b). Although LaNiO_3 and La_2NiO_4 phases were suspected to be formed in this sample, their presence could not be confirmed because of the broadening observed in the peaks. Thus, the DTA peak at 370°C can be attributed to have resulted from the oxidation of nickel. This is in accordance with other observations of a similar exothermic peak between 350 and 400°C for the $\text{Ni} \rightarrow \text{NiO}$ process [14].

The XRD of sample C showed the complete disappearance of the metallic nickel phase and a drastic decrease in the amount of La_2O_3 , indicating conversion of most of the La_2O_3 into LaNiO_3 and La_2NiO_4 phases (Fig. 4c). Sample D (Fig. 4d) indicated a further increase in the intensity of the peaks corresponding to ternary oxide phases and a further decrease (or complete disappearance) of the La_2O_3 signal. Thus, the latter two DTA peaks at around 460°C and 560°C might be the result of exothermic reactions between the simple oxides leading to the formation of ternary phases. All the DTA peaks were very broad in nature because of the slow reactions occurring.

Thermal studies on CaNi_5

In contrast with the LaNi_5 alloy, the thermogram of CaNi_5 (≈ 50 mg) heated in a flow of oxygen at a rate of $10^{\circ}\text{C min}^{-1}$ showed only a small increase in weight (4%) (Fig. 1c). This weight change is much lower than the value expected if the alloy is completely oxidized to CaO and NiO (28.8%).

For the oxidation of calcium alone to CaO, the expected weight change is 4.8%. But, in the present case, not even all the calcium is oxidized. This might be due to the large quantity of the alloy taken. Also, the glow seen with LaNi₅ was not observed, indicating slow oxidation of CaNi₅. A TG run with a small amount of the sample (< 10 mg), and heating to a temperature of 960 °C, resulted in a 12% increase in weight. Although this value still indicates incomplete oxidation of CaNi₅, it can be assumed that, under these conditions, all the calcium has been oxidized to CaO, whereas only a small part of Ni is oxidized to NiO. It is evident that nickel was oxidized to NiO only on prolonged heating (10 h) at 900 °C in a flow of oxygen. Also, the DTA pattern did not show any maxima, thus indicating a slow oxidation process. These observations give confirmation of the results obtained in our earlier work [11].

In the AB₅ type intermetallics, in order to study the effect of element A on the oxidation of nickel, a TG-DTA analysis was carried out on pure nickel powder (< 10 mg). The sample was heated in a flow of oxygen at 10 °C min⁻¹ up to 960 °C. During such a run, only a 4% weight increase was observed. This is much less than the value expected if all the nickel was oxidized to NiO (23.3%). Here again, no DTA peak was observed, indicating a very slow oxidation process.

As discussed earlier, CaNi₅ is oxidized to CaO, Ni and partially to NiO, whereas LaNi₅ is completely oxidized to La₂O₃ and NiO. In order to establish whether the oxide of calcium or lanthanum formed during oxidation influences the oxidation of nickel or the heat evolved during exothermic reaction of calcium or lanthanum with oxygen to form oxides, TG-DTA runs were carried out taking a mixture (< 10 mg) containing La₂O₃ and Ni as well as CaO and Ni. It was found that the amount of nickel oxidized in the presence of CaO or La₂O₃ is not increased significantly over that in the absence of CaO and La₂O₃. This observation confirms that the presence of oxide does not influence the oxidation of nickel and that the large amount of heat evolved during the oxidation of calcium or lanthanum is responsible for the enhanced oxidation of nickel. Since La₂O₃ has a higher enthalpy of formation ($\Delta H_{f,298K}^{\circ} = -1793.7 \text{ kJ mol}^{-1}$) compared with that of CaO ($\Delta H_{f,298K}^{\circ} = -635.1 \text{ kJ mol}^{-1}$), more of the nickel in LaNi₅ became oxidized than in CaNi₅. Formation of ternary oxides is also a cause for the excessive oxidation of nickel in LaNi₅.

CONCLUSION

From the thermal studies on the oxidation behaviour of AB₅ type intermetallics, the following conclusions were reached.

(1) The lanthanum in LaNi₅ is oxidized to La₂O₃ at a much lower temperature compared with the calcium in CaNi₅ to CaO; this has been

attributed to the high ΔG_f° for La_2O_3 ($-1705.8 \text{ kJ mol}^{-1}$) compared with the ΔG_f° for CaO ($-604.2 \text{ kJ mol}^{-1}$).

(2) Two factors contribute to the greater oxidation of nickel in LaNi_5 than in CaNi_5 : (a) the heat evolved during the oxidation of lanthanum to La_2O_3 is very high compared with that of calcium to CaO ; and (b) LaNi_5 may form ternary oxides upon oxidation, whereas this possibility does not exist with CaNi_5 .

(3) In the intermetallics, the two metals are mixed to the atomic level, i.e. the area of contact between the two elements, or the oxide of A and metal B, is very high. This is not the case with a mere mechanical mixture of the oxide of A (La or Ca) and nickel, and hence for such mixtures significant oxidation of nickel was not observed compared with the oxidation of nickel in intermetallics.

ACKNOWLEDGEMENTS

The authors thank the CSIR, New Delhi for the award of a fellowship to two of them (J.C. and M.P.S.). They also acknowledge interesting discussions with Professor G. Aravamudan of I.I.T., Madras, and Professor R.M. Mallya of I.I.Sc, Bangalore.

REFERENCES

- 1 W.E. Wallace, CHEMTECH, (1982) 752.
- 2 J. Barrault, D. Duprez, A. Guilleminot, A. Percheron-Guegan and J.C. Achard, Appl. Catal., 15 (1983) 99.
- 3 V.T. Coon, T. Takeshita, W.E. Wallace and R.S. Craig, J. Phys. Chem., 80 (1976) 1878.
- 4 H. Imamura and W.E. Wallace, J. Catal., 65 (1980) 127.
- 5 M.P. Sridhar Kumar, B. Viswanathan, C.S. Swamy and V. Srinivasan, Catalysis concepts and applications, in B. Viswanathan and A. Meenakshi Sundaram (Eds.), 9th National Symposium on Catalysis, Tata McGraw-Hill, New Delhi.
- 6 C.A. Leungo, A.K. Cabrera, H.B. Mackay and M.P. Maple, J. Catal., 47 (1977) 1.
- 7 M.P. Sridhar Kumar, B. Viswanathan, C.S. Swamy and V. Srinivasan, J. Mater. Sci., 24 (1989) 4387.
- 8 M.P. Sridhar Kumar, B. Viswanathan, C.S. Swamy and V. Srinivasan, Indian J. Chem., 28A (1989) 19.
- 9 J. Barrault, D. Duprez, A. Percheron-Guegan and J.C. Achard, J. Less-Common Met., 89 (1983) 537.
- 10 T. Shiotsuka, K. Onoe and A. Yokoyama, J. Chem. Eng. Jpn., 19 (1986) 519.
- 11 J. Christopher, M.P. Sridhar Kumar and C.S. Swamy, J. Mater. Sci., 23 (1988) 4263.
- 12 C.M. Hay, J.R. Jennings, R.M. Lambert, R.M. Nix, G. Owen and T. Rayment, Appl. Catal., 37 (1988) 291.
- 13 D.M. Nicholes, P. Barnfield and J. Mendham, J. Mater. Sci. Lett., 7 (1988) 304.
- 14 K.M. Vijayakumar, Ph.D. Thesis, IIT, Madras, 1979.