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Studies on the oxidation behaviour of intermetallic compounds

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The oxidation behaviour of the AB_5 type intermetallic compounds $CaNi_5$ and $LaNi_5$ has been studied at different temperatures ranging from 100 to 800° C. The kinetic results indicate that the element A (Ca, La) is first oxidized rapidly followed by slower oxidation of nickel. X-ray diffractograms of the oxidized $LaNi_5$ show the formation of ternary phases like $LaNiO_3$ and La_2NiO_4 at temperature as low as 400° C. A comparison between the oxidation behaviour of the two compounds reveals that $CaNi_5$ is more resistant to oxidation and decomposition than the $LaNi_5$ system.

1. Introduction

In recent years hydrogen-absorbing intermetallic compounds have received much attention for their role in catalysing CO hydrogenation [1] and other reactions [2]. Attention has been focused on the changes that occur in the composition and surface structure of the intermetallic compounds after their use as catalysts in reactions where oxygen-containing reactants are used [3]. There are some reports where the intermetallic compounds are pretreated before being used as catalysts. One of the pretreatment procedures adopted has been the oxidation of the intermetallic compound followed by reduction in a hydrogen atmosphere, resulting in a well-dispersed supported metal catalyst system [4]. These systems are sometimes found to be catalytically more active than the conventionally prepared supported metal catalysts. It is observed that when oxygen-containing reactants are used, bulk oxidation of the intermetallic catalyst occurs resulting in a supported metal system [5].

In view of the vast interest shown in the oxidized/decomposed intermetallics as catalysts (both preoxidized and those oxidized during reaction), it appears to be very important to know the oxidation behaviour of the intermetallic compounds, especially the kinetics of the oxidation process and the various species formed due to oxidation at various temperatures. Identification of the species formed during oxidation is important in ascertaining the active species for the catalytic reaction. Such a study will throw light on the interactions of the active metal species with the support oxides which are responsible for the difference in activity of systems having the same active metal but different oxide supports.

In the present study, the oxidation properties of some RNi_5-type intermetallic compounds (R = Ca, La) have been carried out. Data on the kinetics of oxidation of these compounds at various temperatures are presented and the types of species formed in each case are looked into. Finally, an attempt has been made to compare the behaviour of the systems studied on treatment with oxygen at various temperatures and the relative stabilities in the prevailing atmosphere.

2. Experimental procedure

The intermetallic compounds $CaNi_5$ and $LaNi_5$ were obtained from Ergenics Corportion, USA. The oxidation kinetic studies were done in all-glass static reactor system which could be evacuated to a pressure of 10^{-6} torr. Prior to oxidation the samples were evacuated to 10^{-5} torr at 500° C for 2 h, cooled to the reaction temperature and 1 atm of oxygen admitted. The kinetics of oxidation of the intermetallic compound was followed at constant pressure by measuring the volume of oxygen taken up for a period of 24 h.

For oxidation temperatures greater than 500° C, a tubular furnace was used and oxidation was carried out in a flow of oxygen for 10 h. The X-ray diffractograms of the samples were taken on a Philips PW 1140 X-ray diffractometer.

3. Results and discussion

Kinetic plots for the oxygen uptake by $CaNi_5$ at various temperatures are shown in Fig. 1. The oxidation is seen to be fast in the initial stages. The X-ray diffractograms (Fig. 2) of the samples treated with oxygen at different temperatures for a period of 24 h give an indication as to the nature of the species formed. For the sample treated at 100° C, X-ray diffraction (XRD) shows additional peaks corresponding to Ni (1 1 1) and CaO (2 2 0). As the temperature increases, the intensity of nickel and CaO peaks increases and the intensity of the alloy peaks decreases. The formation of NiO can be clearly observed from the XRD of the sample treated at 400° C. It is seen that even at 500° C the alloy is not completely decomposed.

Fig. 3 shows the kinetics of oxidation of $LaNi_5$ at various temperatures. The type of species formed in each case was determined from the X-ray diffractograms (Fig. 4). It can be clearly seen from Fig. 3 that initially the oxidation is very rapid, as observed in the

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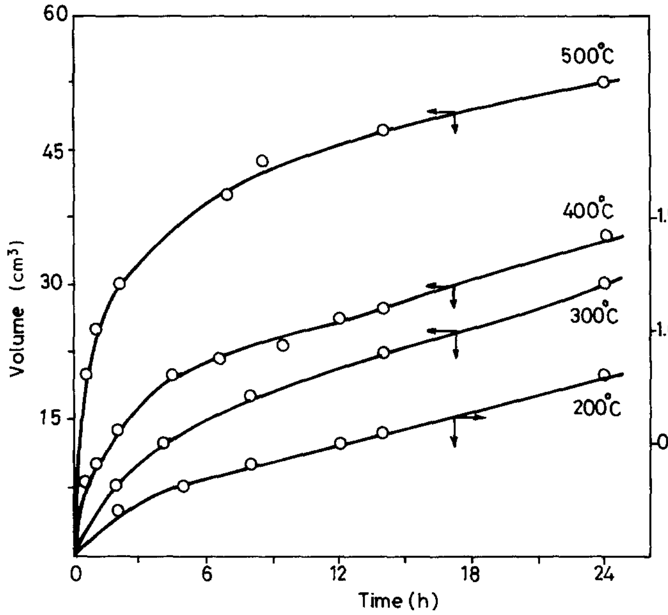

Figure 1 Kinetic plots for the oxidation of $CaNi_5$ alloy at various temperatures. Weight of $CaNi_5$ = 1 g.

case of $CaNi_5$, and then decreases abruptly. It can be understood from Fig. 4 that at 100° C metallic nickel and La_2O_3 are formed and NiO peaks appear for the sample oxidized at 300° C. For the samples oxidized at temperatures of 400° C and above, the XRD patterns indicate the formation of two ternary oxide phases such as perovskite, $LaNiO_3$ and La_2NiO_4, of the K_2NiF_4 type. It is observed that with increase

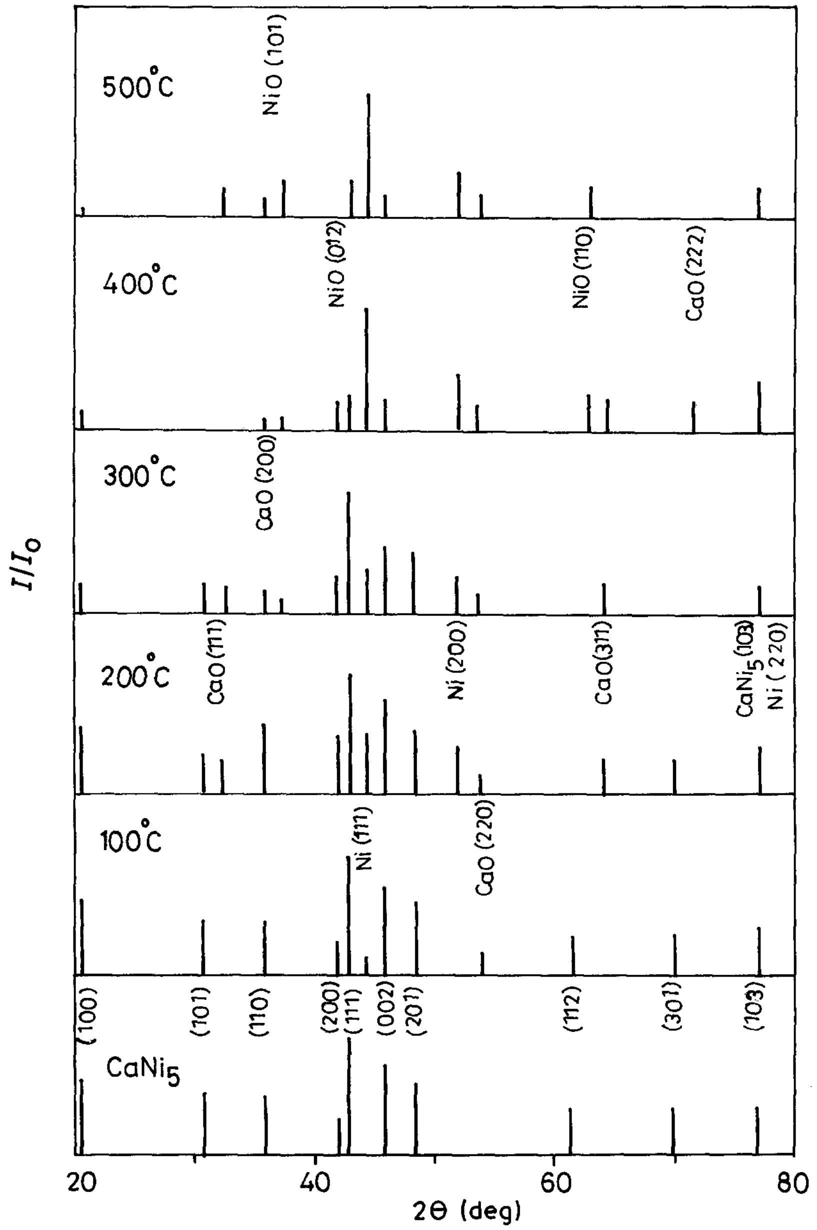

Figure 2 X-ray diffraction patterns of $CaNi_5$ alloy oxidized at various temperatures.

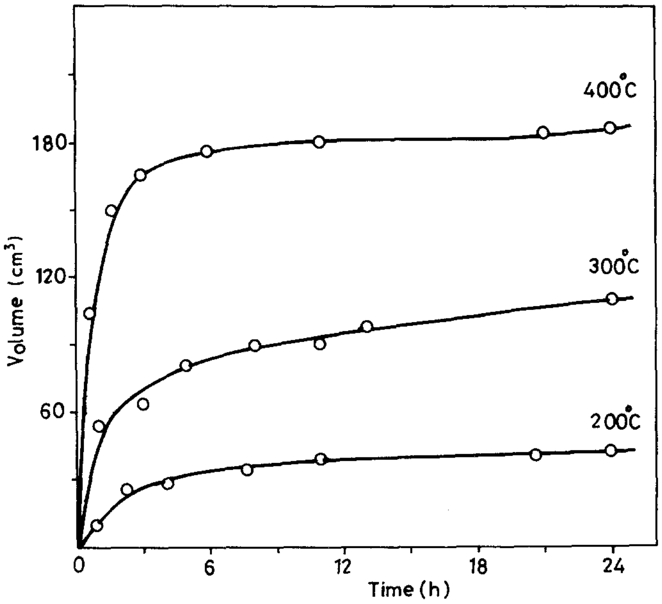

Figure 3 Kinetic plots for the oxidation of $LaNi_5$ alloy at various temperatures. Weight of $LaNi_5$ = 1 g.

in the oxidation temperature, more and more La_2O_3 is converted to ternary oxides, and at a temperature of 600° C the La_2O_3 peaks completely disappear. Formation of the ternary oxides $LaNiO_3$ and La_2NiO_4 have been reported when La_2O_3 and NiO are heated in the presence of oxygen at high temperature [6, 7].

From Figs 1 and 3 it can be seen that the rate of oxidation is rapid in the initial stages and then almost abruptly decreases. This behaviour is observed in both

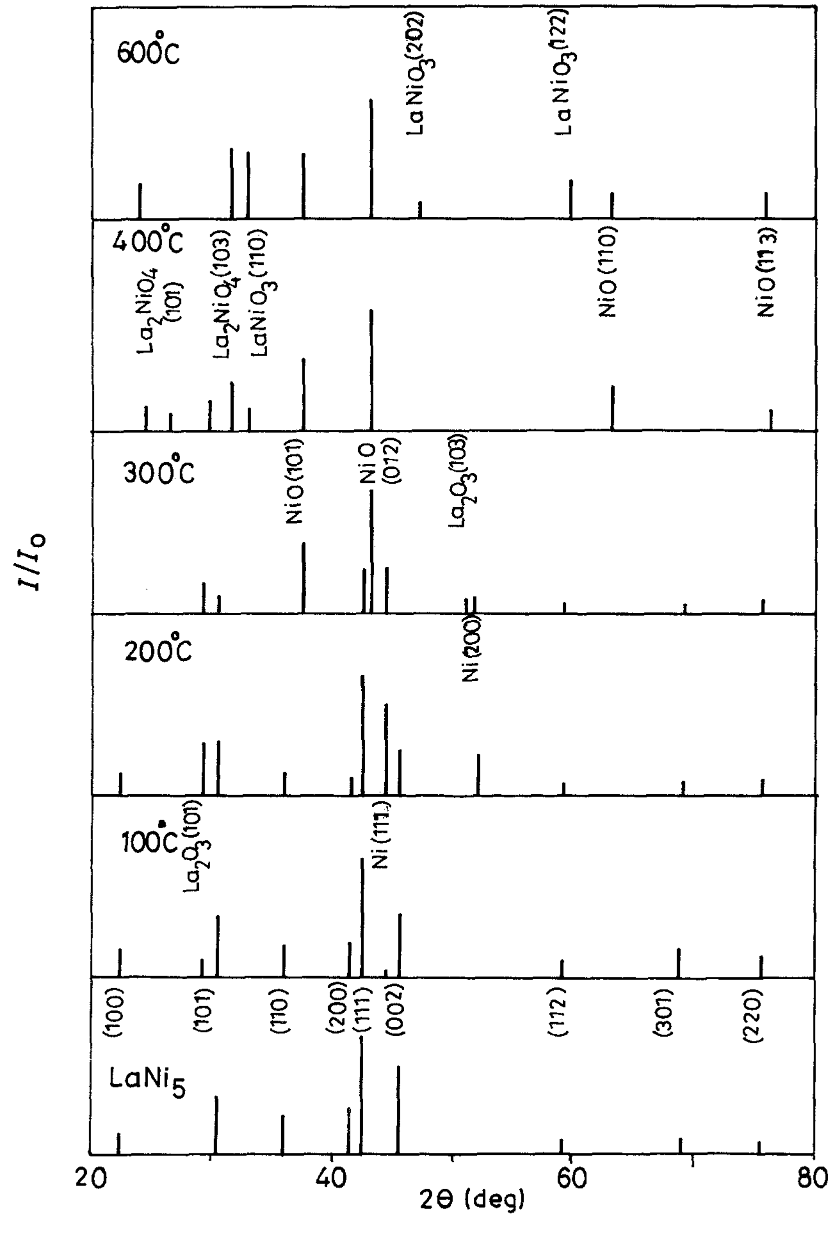

Figure 4 X-ray diffraction patterns of $LaNi_5$ alloy oxidized at various temperatures.

the systems studied. Thus, the oxidation reaction can be divided into a rapid oxidation region and a slow oxidation region. It can be concluded by analysing Figs 2 and 4 that initially lanthanum (or calcium) is rapidly oxidized to La_2O_3 (or CaO) and then nickel is oxidized to NiO at a slower rate.

Figs 1 and 2 also reveal that the rate of oxidation of $LaNi_5$ is much faster compared to that of $CaNi_5$. This difference in behaviour of the two systems can readily be explained on the basis of the free energy of formation of the respective oxides. The strong affinity of lanthanum for oxygen is shown by the high $\Delta G^0_{298\,K}$ value ($-1254.2\,kJ\,mol^{-1}$) for the formation of La_2O_3 as compared to that of CaO ($\Delta G^0_{298\,K} = -144.4\,kJ\,mol^{-1}$). This is also evidenced from the observation that the $LaNi_5$ sample is completely oxidized (as indicated by the disappearance of $LaNi_5$ peaks in XRD) at temperatures below 400° C, whereas the oxidation of $CaNi_5$ continues up to temperatures greater than 500° C.

One other interesting observation from these studies is the formation of $LaNiO_3$ and La_2NiO_4 phases in the oxidation of $LaNi_5$ at 400° C. The low free energy of formation of $LaNiO_3$ from La_2O_3 and NiO ($\Delta G^0_{1273\,K} = -10.1\,kJ\,mol^{-1}$) [8] explains this observation. It is also seen that even at temperatures less than 600° C (Fig. 4) all the La_2O_3 is converted to $LaNiO_3$ and La_2NiO_4, leaving the excess nickel as NiO. It is known that $LaNiO_3$ functions as a very good catalyst for redox reactions like CO oxidation [9] and N_2O decomposition [6]. Demazeau *et al.* [10] observed that the $LaNiO_3$ phase when heated at high temperature leads to the formation of La_2NiO_4, which again is a very stable and efficient catalyst for redox reactions [7, 11].

It is interesting to note that in the present case, the ternary oxides $LaNiO_3$ and La_2NiO_4 are formed at temperatures much lower than those reported for their formation from component oxides. This may be due to the fact that in the present case, since we start with the alloy, the corresponding oxides formed during oxidation are in a finely divided state and hence very reactive. These ternary oxides, on reduction in the presence of hydrogen at temperatures of 400 to 600° C, are converted to the metal supported on oxide systems [12].

There has so far been no report about the formation of the ternary phase, of the type $CaTiO_3$ or K_2NiF_4, in the Ca–Ni–O system. This is because of the unfavourable tolerance factor [13] or the radius ratio [14] required in the Ca–Ni–O system for the formation of the above phases. Hence, in the present study, the absence of a ternary phase in the oxidized $CaNi_5$ system can be understood.

The oxidation behaviour of $CaNi_5$ and $LaNi_5$ systems is also different in the disappearance of the metallic nickel. With $LaNi_5$, the entire nickel present is converted to NiO at temperature less than 400° C, whereas in the case of $CaNi_5$, most of the nickel is present in the metallic form, even at temperatures greater than 500° C. $CaNi_5$ is completely oxidized to CaO and NiO only at temperatures greater than 800° C in the presence of oxygen. One possible reason for such a vast different in the appearance of metallic nickel in the oxidized $CaNi_5$ and $LaNi_5$ may be the consumption of metallic nickel, in the latter case, for the formation of the ternary oxides.

4. Conclusion

From the above observations it can be expected that in hydrogenation/dehydrogenation reactions on these intermetallics, when oxygen-containing reactants are used, the $LaNi_5$ will decompose much more easily than $CaNi_5$ to the component oxides or metal–oxide mixtures. The oxidized $LaNi_5$ system appears to be a very good catalyst for various types of reaction, keeping in mind the different phases formed during the course of oxidation. In contrast, the oxidized $CaNi_5$ system could form a very stable supported metal system and function as a catalyst for hydrogenation and dehydrogenation reactions.

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