A Stepwise Selective Chlorination-Chemical Vapor Transport Reaction for Rare Earth Separation

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A stepwise selective chlorination-chemical vapor transport reaction results in the efficient separation of neighboring rare earth elements La, Ce, Pr, and Nd from their binary oxide mixtures.

Rare earth vapor complexes have been studied as model systems to understand the nature of rare earth elements in their complexes due to the negligible molecular interactions.[1] They have also been investigated for many possible applications. For instance, Adachi and co-workers have recently developed a chemical vapor transport (CVT) process for the separation[2,3] and recovery[4] of rare earth elements via vapor complexes. The results showed that this dry process has many advantages over the conventional wet processes. On the other hand, we have compared the mutual separation characteristics for neighboring rare earth elements La, Ce, Pr, and Nd from binary[5] and quaternary[6] chloride mixtures and oxide mixtures under identical CVT reaction conditions. The results showed that the separation was more efficient from the oxide mixtures than from the chloride mixtures. In all these cases[2-6] both chlorination and CVT were carried out almost at the same time at high temperature for 6-82 h. In this letter, we tried to combine the selective chlorination (SC) at low temperature together with the CVT at high temperature to separate La, Ce, Pr, and Nd from their binary oxide mixtures.

The chemicals, experimental apparatus and procedure used in this study are the same as those used previously[5,6] except for the details noted below. A raw material was formed by mixing active carbon with a binary oxide mixture at an atomic ratio of C:Ln:Ln' = 6:1:1.

Let T denote the highest temperature in the tube reactor, where the raw material placed. The raw material was chlorinated by dry Cl_2 gas with a flow rate of 20 $cm^3 \cdot min^{-1}$ at T = 800 K for 2 h. Within the temperature range of T = 800-1300 K, the Cl_2 gas was replaced by a dry CO-HCl mixed gas with the flow rates of 40 and 20 $cm^3 \cdot min^{-1}$, respectively. The rare earth chlorides produced were then transported with $AlCl_3$ at T = 1300 K for 6 h, using a dry CO gas with a flow rate of 40 $cm^3 \cdot min^{-1}$ as carried gas. During the whole reaction, a given pressure gradient was maintained by a subatmospheric pressure of 2.7 kPa at the outlet of the tube reactor. A temperature gradient used in the CVT sub-reaction is shown in Fig. 1.

Figures 1A-1C show the reaction results of the three binary oxide mixtures La_2O_3-CeO_2, CeO_2-Pr_6O_{11}, and Pr_6O_{11}-Nd_2O_3 in the form of deposition profiles for the rare earth chlorides vs. fraction numbers (FN) of the receptors. Table 1 lists the separation factor obtained. As compared with our previous study,[5] the new reaction resulted in a significant CVT yield for every oxide mixture, an increase in separation factor from 21.4[5] to 28.3 for La:Ce and from $\geqslant 100^5$ to $\geqslant 200$ for Pr:Ce and a

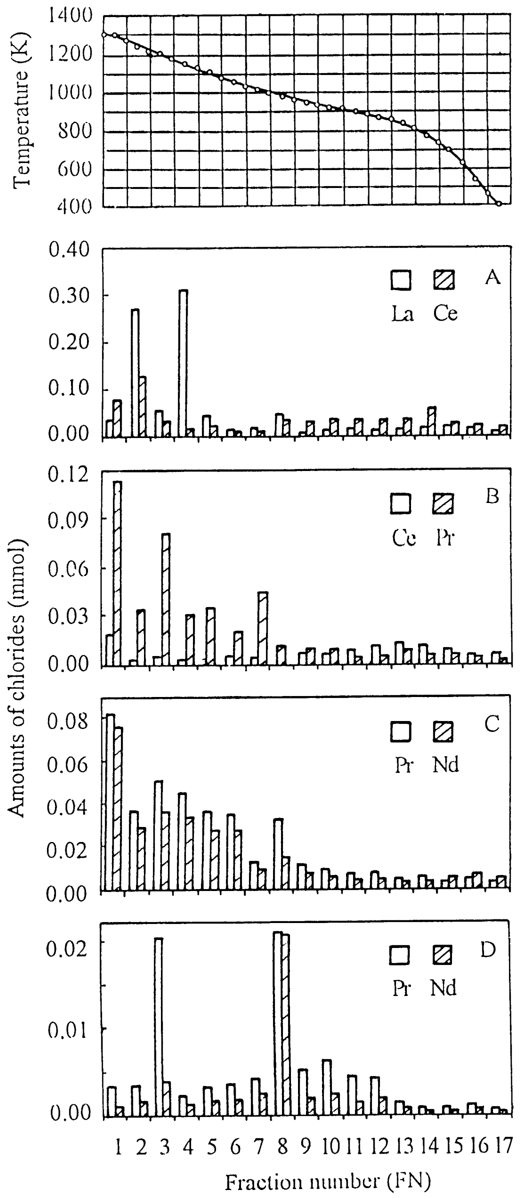

Figure 1. Temperature dependence curve, and distribution of $LaCl_3$, $CeCl_3$, $PrCl_3$, and $NdCl_3$ deposits in a stepwise SC-CVT reaction formed from the binary oxide mixtures: (A) La_2O_3-CeO_2, (B) CeO_2-Pr_6O_{11}, (C) Pr_6O_{11}-Nd_2O_3, and (D) Pr_6O_{11}-Nd_2O_3. The SC was mainly realized with Cl_2 gas at T = 800 K for 2 h and the CVT was carried out with $AlCl_3$ at T = 1300 K for 6 h either under a CO atmosphere for (A)-(C) or under an Ar atmosphere for (D).

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Table 1. The separation factors between neighboring rare earth elements La, Ce, Pr and Nd from their binary oxide mixtures in a stepwise SC-CVT reaction, using $AlCl_3$ as complex former

	SF[a]	FN[b]		CVT carried gas
La_2O_3-CeO_2	28.3	4	(La:Ce)	CO
CeO_2-Pr_6O_{11}	$\geqslant 200$	5	(Pr:Ce)	CO
Pr_6O_{11}-Nd_2O_3	1.74	8	(Pr:Nd)	CO
Pr_6O_{11}-Nd_2O_3	4.35	3	(Pr:Nd)	Ar

[a]SF = separation factor; [b]FN = fraction number.

slight decrease in that from 1.84[5] to 1.74 for Pr:Nd. It seems difficult to explain these changes at the present stage. However, our preliminary experiments showed that the SC sub-reaction of the raw materials with dry Cl_2 gas at T = 800 K for 2h might result in an yield of 18-99 % for the four rare earth elements and a separation factor of 3.64 for La:Ce, 2.82 for Pr:Ce, and 1.10 for Pr:Nd, and that both the dry CO-HCl mixed gas within the temperature range of T = 800-1300 K and dry CO-Al_2Cl_6 mixed gas at T = 1300 K might prevent the formation of rare earth oxychlorides from their oxides and chlorides. Moreover, the complexation reaction of CO gas not only with rare earth fluorides[7] but also with some other metal chlorides[8] would suggest the possibility of the reaction between CO and rare earth chlorides in this study. Furthermore, the high CO partial pressure in the CVT sub-reaction at T = 1300 K might result in an increase in the separation factors for La:Ce, Pr:Ce, and Nd:Pr accordimg to the exchange reactions (1)-(3) between the coexistent oxides and chlorides:

$$(1/2)La_2O_3(s) + CeCl_3(l) + (1/2)CO(g) = LaCl_3(l) + CeO_2(s) + (1/2)C(s), \tag{1}$$

$$CeO_2(s) + PrCl_3(l) + (1/6)C(s) = CeCl_3(l) + (1/6)Pr_6O_{11}(s) + (1/6)CO(g), \tag{2}$$

$$(1/6)Pr_6O_{11}(s) + NdCl_3(l) + (1/3)C(s) = PrCl_3(l) + (1/2)Nd_2O_3(s) + (1/3)CO(g). \tag{3}$$

Figure 1D shows the reaction results for the binary oxide mixture Pr_6O_{11}-Nd_2O_3 under an other condition where a dry Ar gas with a flow rate of 40 $cm^3 \cdot min^{-1}$ instead of the CO gas was used as carried gas in the CVT sub-reaction. A relatively low CVT yield was obtained but the separation factor increased to 4.35 for Pr:Nd as listed in Table 1. They might be caused by a relatively low CO partial pressure in the Ar atomsphere. The mutual separation between other neighboring rare earth elements using the stepwise SC-CVT reaction is in progress.

In conclusion, a stepwise SC-CVT reaction developed in this study allows both chlorination and CVT to be realized at different conditions, resulting in relatively high reaction yield and relatively efficient separation for the neighboring rare earth elements La, Ce, Pr, and Nd from their binary oxide mixtures. This stepwise reaction should also be suitable for the extraction and separation of rare earths directly from concentrates of their minerals and for the rare earth recovery.

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References and Notes

1 Z.-C. Wang and L.-S. Wang, *Inorg. Chem.*, **36**, 1536 (1997), and references cited therein.

2 G. Adachi, S. Shinozaki, Y. Hirashima, and K. Machida, *J. Less-Common Met.*, **169**, L1 (1991); G. Adachi, K. Murase, S. Shinozaki, and K. Machida, *Chem. Lett.*, **1992**, 511; K. Murase, S. Shinozaki, K. Machida, and G. Adachi, *Bull. Chem. Soc. Jpn.*, **65**, 2724 (1992); K. Murase, S. Shinozaki, Y. Hirashima, K. Machida, and G. Adachi, *J. Alloys Comp.*, **198**, 31 (1993).

3 K. Murase, K. Machida, and G. Adachi, *Chem. Lett.*, **1994**, 1297; K. Murase, T. Ozaki, K. Machida, and G. Adachi, *J. Alloys Comp.*, **233**, 96 (1996); T. Ozaki, T. Miyazawa, K. Murase, K. Machida, and G. Adachi, *J. Alloys Comp.*, **245**, 10 (1996); T. Ozaki, K. Murase, K. Machida, and G. Adachi, *Trans. Inst. Min. Metall.*, **105**, C141 (1996).

4 K. Murase, K. Machida, and G. Adachi, *Chem. Lett.*, **1994**, 1555 ; K. Murase, K. Machida, and G. Adachi, *J. Alloys Comp.*, **217**, 218 (1995).

5 Z.-C. Wang, J. Yu, and Y.-L. Yu, *Bull. Chem. Soc. Jpn.*, **69**, 2369 (1996).

6 Z.-C. Wang, J. Yu, Y.-L. Yu, and Y.-H. Sun, *J. Alloys Comp.*, (Paper No: A97031, in press).

7 R. H. Hauge, S. G. Gransden, and J. L. Margrave, in "Proceedings of the Symposium of High Temperature Metal Halide Chemistry", ed by D. L. Hildenbrand and D. D. Cubicciotti, The Electrochemical Society, Inc., Princeton (1978), p. 310.

8 D. A. Van Leirsburg and C. W. Dekock, *J. Phys. Chem.*, **78**, 134 (1974); D. Tevault and K. Nakamoto, *Inorg. Chem.*, **15**, 1282 (1976).