JOURNAL OF CATALYSIS 42, 60–72 (1976)

Catalytic Activity of Lanthanide Oxides in Oxidation of Butane

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Received May 28, 1975

The catalytic oxidation of butane was studied over a series of lanthanide oxides in order to investigate the effect of the electronic configuration on the catalytic activity. Lanthanum oxide was one of the least active catalysts. Cerium oxide was the most active one, and the activity decreased with an increase in the atomic number from cerium to gadolinium. The activity of terbium oxide was the second highest, and again the activity decreased from terbium to lutetium. Such a dependence of the activity on the atomic number was in good agreement with the electrical conductivity, and in fair agreement with the heat of formation of oxide. The dependences of the electrical conductivity and the heat of formation could be related to the stability of the tetravalent ion, to which the catalytic activity also could be related by assuming that the rate determining step is the oxidation of the trivalent ion to the tetravalent ion. A good correlation was obtained between the catalytic activity and the fourth ionization potential as a measure of the stability of the tetravalent ion relative to the trivalent ion. On referring to the correlation, the dependence of the catalytic activity on the atomic number was interpreted in terms of two factors based on the electronic configuration of the 4*f* subshell, i.e., the Coulomb attraction energy between the Xe shell and the 4*f* electron, and the exchange energy between the 4*f* electrons.

INTRODUCTION

Some of the properties of lanthanum and the succeeding 14 lanthanide elements have been explained on the basis of the electronic configuration. The normal valence of the lanthanide ions is tripositive. The trivalent ion of lanthanum has the electronic configuration of the closed Xe shell, and the succeeding elements successively add 14 electrons to the inner 4*f* subshell. The electronic configuration of the outer subshell is $5s^25p^6$ for all the ions. The outer subshell of the tetra- and divalent ions remains $5s^25p^6$. The magnetic properties of the lanthanide ions depend on the electron structure of the 4*f* subshell, and therefore differs from each other. On the other hand, the chemical properties are quite similar to each other, because the 4*f* orbital does not contribute significantly to the chemical bond of the lanthanide compounds (*1*, *2*).

It has been said that the same is true for the catalytic properties of the lanthanide oxides. The catalytic activity differs from each other in such a reaction as the parahydrogen conversion which proceeds by the paramagnetic mechanism (*3*). On the other hand, the difference in the activity is rather small in the reaction where the chemical bond is formed between the reactant and the catalyst surface (*4*).

In the last several years, however, it has been found in a series of the catalytic oxidation that the catalytic activity of the lanthanide oxides significantly differs from each other. Sazonov and co-workers (*5*) measured the activation energies of the isotopic exchange of oxygen and of the desorption of carbon dioxide in the oxidation of carbon monoxide, and found that the dependences of the activation energies on the atomic number were similar to that of the magnetic moment. Minachev (*6*) compared the catalytic activity in the oxidation of hydrogen and propylene with that in the isotopic exchange of oxygen, and suggested that the catalytic activity depends on the binding energy of oxygen with the surface and on the valence of the lanthanide ions. Bakumenko and Chashenikova (*7*) found in the oxidation of hydrogen that the activity of neodymium and erbium oxides was lower than cerium, praseodymium, and terbium oxides with the tetravalent ion, which was explained on the basis of the heat of formation of oxide. Lazukin and co-workers (*8*) found a good correlation between the activation energy of the oxidation of propylene and that of the electrical conductivity, and concluded that the electron transfer from the reactant or the intermediate to the catalyst surface is involved in the rate determining step. Some of the authors (*5, 6*) suggested from these results that the catalytic activity of the lanthanide oxides depends on the electronic configuration of the inner 4*f* subshell.

The purpose of the present study is to clarify the detailed mechanism of the effect of the electronic configuration of the inner 4*f* subshell on the catalytic activity of the lanthanide oxides, using for an example the oxidation of butane. In general, the catalytic activity depends on a number of factors, and therefore it is difficult to clarify the exact nature of the catalytic activity. Using a series of catalysts with similar chemical properties, such as the lanthanide oxides, more exact conclusions can be expected.

EXPERIMENTAL METHODS

The catalysts were the supported oxides of the lanthanum series except promethium on an α-alumina. The α-alumina was impregnated in 1 *N* solutions of lanthanide nitrates, evaporated to dryness on a water bath, dried at 110°C overnight, and calcined at 500°C for 2 hr in a stream of air. The concentration of lanthanide oxides on the support was 0.1 g of the sesquioxide/g of α-alumina. The lanthanide nitrates were supplied from Shin-Etsu Chemical Industry Co., and were stated to be of 99.9% purity or better. The α-alumina was obtained by the calcination of an activated alumina (KAT-6 from Sumitomo Chemical Industry Co.) at 1200°C for 24 hr, and was identified as α-alumina by X-ray diffraction pattern. BET surface area of the α-alumina was 4.9 $m^2\ g^{-1}$. In the standard reaction condition, 1 g of the catalyst, i.e., 0.091 g of the lanthanide sesquioxide supported on 0.909 g of the α-alumina, was used.

The catalytic activity was measured by using a conventional flow reactor at atmospheric pressure. The catalyst was packed in the U-tube reactor made of Pyrex glass with an inside diameter of 4 mm. The reactor was installed in a fluidized bath with an electrically heated wire in order to heat the catalyst bed uniformly. Butane used as a reactant contained 97.2% of *n*-butane, 0.4% or 1-butene, 1.5% of *trans*-2-butene, and 0.9% of *cis*-2-butene. Air from a conventional pneumatic compressor was used as another reactant after being purified by passage through a glass wool layer and a silica gel column. Butane and air were passed downward through the catalyst bed at the fixed flow rate of 0.167 and 0.83 $\mu m^3\ sec^{-1}$, respectively. It will be expected that the characteristics of the catalyst in the oxidation can be most easily understood in a highly reducing atmosphere.

The analysis of the reaction products was made by the gas chromatography with a 10 m column of 30 wt% γ-butyrolactone on C-22, a 2 m column of Porapack Q, and a 2.5 m column of molecular sieve 13X at room temperature.

RESULTS

The following reaction products were observed: carbon dioxide, carbon monoxide, methane, ethylene, propylene, and 1-, *trans*-2-, and *cis*-2-butenes. Only a slight amount of butadiene was observed in all cases, and therefore it was neglected. The products were divided into four groups: carbon dioxide, carbon monoxide, cracking products (methane, ethylene, and propylene), and butene isomers, and the yield of each group was used to show the experimental results.

Table 1 shows the results of the noncatalytic reaction. When the reactor was empty, the yields of carbon dioxide and carbon monoxide were only less than 0.4%. But those of cracking products and butenes could not be neglected. When the reactor was packed with the α-alumina used as the support, the yield of butenes was less than that in the former case, and the yield of cracking products was approximately the same as that in the former case. The yields of carbon dioxide and carbon monoxide at 500°C were larger than those in the former case, but the difference between the two cases was not so large. It follows that the α-alumina seems to have only a little effect on the oxidation into carbon dioxide and carbon monoxide at 500°C, and no effect on the other reactions.

TABLE 1

Results of the Noncatalytic Reaction

Packing in reactor	Temp. (°C)	Yield (%)			
		Butenes	C_1–C_3	CO	CO_2
Empty	500	3.12	1.05	0.25	0.43
	450	2.09	0.82	0.35	0.34
	400	1.58	0.51	Tr	0.11
α-Alumina	500	2.62	1.39	0.88	1.16
	450	1.60	0.59	0.35	0.45
	400	0.76	0.32	Tr	0.06

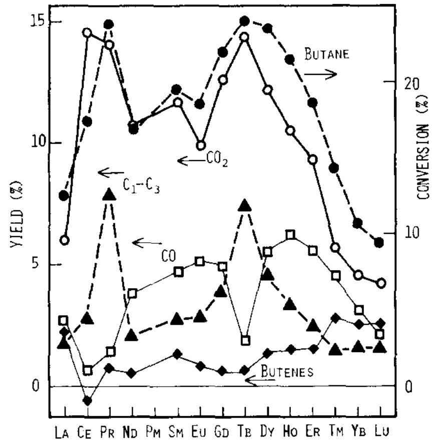

FIG. 1. Conversion and yields at 500°C.

Figure 1 shows the dependence of the conversion and the yields at 500°C on the atomic number of the lanthanides. As a whole, the yield of carbon dioxide was the highest, and the yields of carbon monoxide and cracking products were next to it. The yields of butenes were only less than 3%. The conversion and the yields were significantly different from one catalyst to the others. The conversion was the highest on praseodymium oxide and the second highest on terbium oxide. It was reported that these oxides show the highest activity in the isotopic exchange of oxygen and in the oxidation of hydrogen (*6*). The yield of carbon dioxide showed the similar tendency to the conversion except that the highest activity was observed on cerium oxide, but not on praseodymium oxide. It was reported that cerium and terbium oxides show the highest activity in the oxidation of propylene (*6*). The yield of carbon monoxide varied with the atomic number in the opposite direction to that of carbon dioxide between lanthanum and holmium, and in the same direction between erbium and lutetium. The yield of cracking products was the highest on praseodymium and terbium oxides similarly to the conversion. But the difference between the highest yield and the others was more marked than that in the conversion. The tendency of the butene yield was not obvious, because the yield was less than that of the noncatalytic reaction shown in Table 1. The negative yield of butenes on cerium oxide indicates that butenes involved in the reactant were converted.

Figure 2 shows the results at 450°C. The conversion and the yield of carbon dioxide varied in the similar manner to each other with the atomic number. They were significantly low on lanthanum oxide, were the highest on cerium oxide, decreased with an increase in the atomic number from cerium to gadolinium, were the second highest on terbium oxide, and again decreased from terbium to lutetium. Most of the yields of carbon monoxide, cracking products, and butene isomers were only less than 2%, and therefore a clear tendency could not be observed. The results at 400°C in Fig. 3 show the similar tendency to those at 450°C in Fig. 2, except that the difference between the highest activity of cerium oxide and the others was more marked than that at 450°C.

At 400 and 450°C, the main product was carbon dioxide, as shown in Figs. 2 and 3. While, at 500°C, the yields of carbon monoxide and cracking products were considerably large. In order to ascertain which of the yields is the most suitable measure of the catalytic activity, the effect of the catalyst weight on the yield of each group was examined. In Fig. 4a, the α-alumina was packed on and below the catalyst bed. The sum of the catalyst and the α-alumina was 1 g. As mentioned above, the α-alumina has a slight effect only on the oxidation into carbon dioxide and carbon monoxide. When the catalyst weight was 0.063 g, the yields of carbon dioxide and the cracking products were approximately 10 times, and the yield of carbon

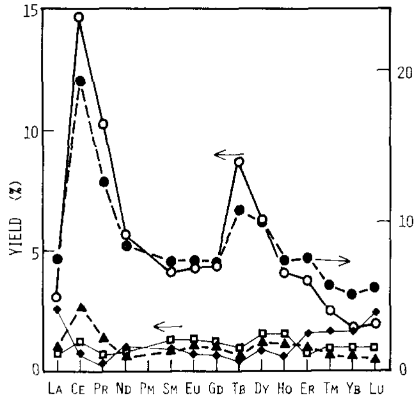

Fig. 2. Conversion and yields at 450°C (for the symbols see Fig. 1).

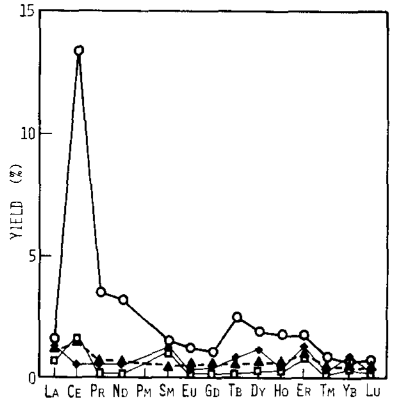

Fig. 3. Yields at 400°C (for the symbols see Fig. 1).

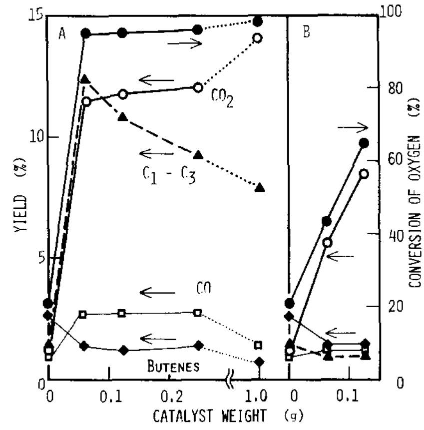

Fig. 4. Effect of catalyst weight (500°C, praseodymium). (A) α-Alumina was loaded on and below the catalyst bed. (B) Catalyst particles were dispersed in α-alumina bed.

monoxide was 3 times as much as those without the catalyst. The yield of butenes, on the contrary, decreased to near half of that without the catalyst. The yield of carbon dioxide only slightly increased with the catalyst weight up to 1 g. In contrast, the yield of the cracking products decreased, and the yields of carbon monoxide and butenes also seemed to decrease. The conversion of oxygen already reached 95% at 0.063 g, and increased only slightly with the catalyst weight. Figure 4b shows the results obtained in the case where the catalyst particles were dispersed in the α-alumina bed. The sum of the catalyst and the α-alumina was 1 g. The conversion of oxygen and the yield of carbon dioxide monotonously increased with the catalyst weight. The yield of carbon monoxide also increased, but only slightly. The yields of cracking products and butenes decreased with an increase in the catalyst weight.

The difference between Fig. 4a and b can be interpreted as follows: in the case of Fig. 4a, the complete oxidation to carbon dioxide proceeded with violence and the temperature of the catalyst bed increased markedly, which resulted in the higher yields of cracking products and carbon monoxide than those without the catalyst. In order to ascertain such a hypothesis, the temperature of the catalyst bed was measured with a thermocouple embedded in the catalyst bed. In the case of Fig. 4a, the bed temperature was 55°C higher than the fluidized bath, while, in the case of Fig. 4b, the difference in the temperature was only less than 5°C. It follows that the high yields of cracking products and carbon monoxide in Fig. 4a were caused by the elevated temperature, but not by the catalysis, and that these yields cannot be a measure of the catalytic activity because these yields were higher than those without the catalyst in Fig. 4a where the temperature increased markedly, and less in Fig. 4b where the temperature increase was negligible. The yield of butenes also cannot represent the activity, because it was less than that without the catalyst in Fig. 4b. The yield of carbon dioxide is suitable to represent the catalytic activity. It increased monotonously with the catalyst weight in Fig. 4b, and carbon dioxide was the main product at 400 and 450°C. But the yield at 500°C in Fig. 1 is not suitable, because the conversion of oxygen was larger than 80% on most of the catalysts in Fig. 1. After all, the yield of carbon dioxide at 400 or 450°C is the most suitable measure of the catalytic activity. The conversion of oxygen was less than 55% except for cerium oxide (97.7%) and praseodymium oxide (74.2%) at 450°C, and less than 30% except for cerium oxide (97.8%) at 400°C.

DISCUSSION

The Catalytic Activity and Some Properties of Lanthanide Oxides

As mentioned above, the catalytic activity of the lanthanide oxides in the oxidation of butane can be represented by the yield of carbon dioxide at 400 or 450°C in Figs. 2 or 3. Lanthanum oxide was one of the least active catalysts, and cerium oxide was the most active. The activity decreased as the atomic number increased on going from cerium to gadolinium. The activity was the second highest on terbium oxide, and again decreased on going to lutetium oxide. The comparison will hereinafter be made between the above-mentioned variation of the catalytic activity with the atomic number and that of some physical and chemical properties of the lanthanides.

It is well known that the magnetic property of the lanthanide ions differs from one element to the other. Figure 5 shows the magnetic moment of the trivalent lanthanide ions. Sazonov and coworkers (*5*) concluded that the electron structure of the 4*f* subshell has an effect on the isotopic exchange of oxygen and the oxidation of carbon monoxide, because the

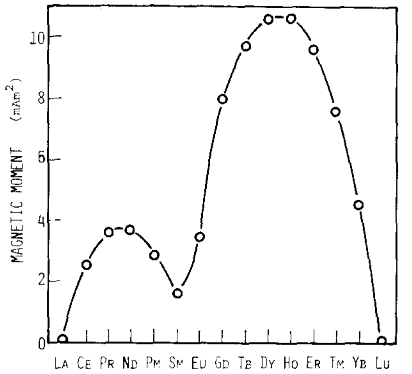

Fig. 5. Magnetic moment of trivalent ion of lanthanide (*1*).

plots of the activation energies of both reactions against the atomic number were similar to that of the magnetic moment shown in Fig. 5. Figure 5 is similar to the plot of the conversion at 500°C shown in Fig. 1 in respect that the maximums are observed near praseodymium and dysprosium, but the results at 500°C cannot represent the quantitative activity as mentioned above. The plot of the yield of carbon dioxide at 400 and 450°C which can be a measure of the catalytic activity is significantly different from that of the magnetic moment: First, the yield was the highest on cerium and terbium oxides, but not on dysprosium and neodymium oxides as the magnetic moment. Second, the catalytic activity of the oxides between cerium and gadolinium was, as a whole, higher than that between terbium and lutetium, contrary to the magnetic moment. The difference in the dependence on the atomic number between the catalytic activity and the magnetic moment cannot be explained by the difference in the oxidation state of the lanthanide ions. The usual valences of cerium and lanthanum ions are tetra- and tripositive. The tetravalent cerium ion and the trivalent lanthanum ion have the same electronic configuration ($4f^0 5s^2 5p^6$), and therefore approximately the same magnetic moment (*1*). On the other hand, cerium oxide was the most active catalyst, though lanthanum oxide was one of the least active catalysts. It follows that the discussion made by Sazonov and co-workers (*5*) cannot be applied to the present case.

Morooka and Ozaki (*9*) measured the catalytic activity of a variety of oxides in the oxidation of several hydrocarbons, and found a good correlation between the catalytic activity and the heat of formation of oxide per g-atom of oxygen. Bakumenko and Chashenikova (*7*) also found a correlation between the heat of formation and the catalytic activity in the oxidation of hydrogen on some lanthanide oxides. Figure 6 shows the heat of formation of the lanthanide oxides per g-atom of oxygen (*10, 11*). The heat of formation of the sesquioxides is not so much different from each other. The heat of formation of the higher oxides per g-atom of oxygen is lower than that of the sesquioxides, which is in good agreement with the higher activity of cerium, praseodymium, and terbium oxides. But the heat of formation cannot interpret the difference in the catalytic activity among the higher oxides and among the sesquioxides. The higher oxides of neodymium and dysprosium have not been known, but the existence of the tetravalent ions of neodymium and dysprosium has been confirmed. It is possible

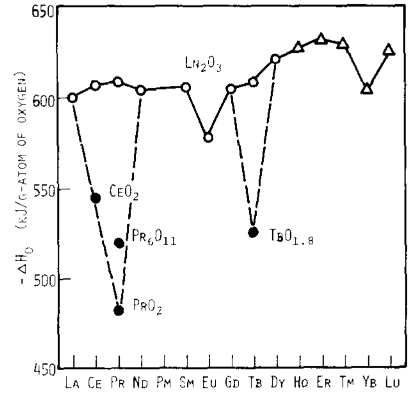

Fig. 6. Heat of formation of lanthanide oxide per g-atom of oxygen (○, ●) Ref. (*10*); (△) Ref. (*11*).

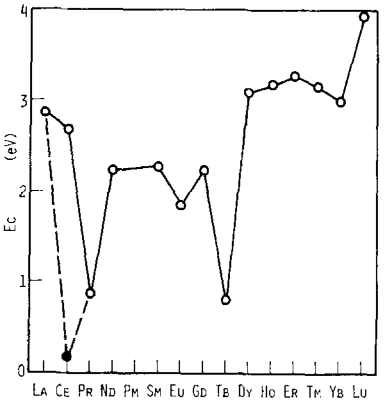

FIG. 7. Activation energy of electrical conductivity of lanthanide oxide (○) Ref. (*13*); (●) Ref. (*14*); 1 eV ≃ 1.602 × 10^{-19} J.

that a small amount of the tetravalent ion is present in the sesquioxides of neodymium and dysprosium and is the origin of the high activity next to the higher oxides. If so, the catalytic activity can be attributed to the stability of the tetravalent ion.

Krylov (*12*) found good correlations between the width of the forbidden zone and the catalytic activity of the oxide catalyst in several reactions. Lazukin and co-workers (*8*) also found a good correlation between the activation energy of the electrical conductivity and that of the oxidation of propylene on the lanthanide oxides. The open circles in Fig. 7 show the activation energy of the electrical conductivity of the lanthanide oxides obtained by Bogoroditskii and co-workers (*13*), and it depends on the atomic number almost in the opposite direction to the yield of carbon dioxide at 450°C. A good correlation will be obtained between the two, except for cerium oxide. Blumenthal and co-workers (*14*) measured the electrical conductivity of cerium dioxide over the oxygen pressure region 1 to 10^{-21} atm, and obtained quite a small activation energy shown by the solid circle in Fig. 7, which corresponds well to the highest activity of cerium oxide. The experimental condition in the present study is a significantly reducing one, and is close to that of Blumenthal and co-workers (*14*). The conduction mechanism of the cerium (*14*), praseodymium (*15*), and terbium (*16*) oxides has been said to be "hopping type," that is, the current is carried by a rapid electron switch process between the trivalent ion and the tetravalent ion. Therefore, high electrical conductivity of these oxides can be attributed to the high concentration of both ions (*15, 16*). The electrical conductivity of the lanthanide sesquioxides also may be attributed to the tetravalent ion, because the lanthanide sesquioxides are *p*-type semiconductors in the presence of oxygen (*16*). If so, the correlation between the electrical conductivity and the catalytic activity seems to suggest that the catalytic activity also may be attributed to the stability of the tetravalent ion.

The Catalytic Activity and the Stability of the Tetravalent Ion

As mentioned above, the catalytic activity of the lanthanide oxides seems to be attributed to the stability of the tetravalent ion. The relation between the two can be interpreted in the following manner. The oxidation of carbon monoxide on cerium dioxide has been said to proceed via the successive oxidations and reductions of the catalyst surface (*17*). Assuming the "redox mechanism," the oxidation of butane can be divided into the following two steps.

$$2\,\mathrm{Ln}^{3+} + \tfrac{1}{2}\mathrm{O}_2 \rightarrow 2\,\mathrm{Ln}^{4+} + \mathrm{O}^{2-}, \qquad (1)$$

$$2\,\mathrm{Ln}^{4+} + \mathrm{O}^{2-} + a\cdot\mathrm{C}_4\mathrm{K}_{10} \rightarrow 2\,\mathrm{Ln}^{3+} + b\cdot\mathrm{CO}_2 + c\cdot\mathrm{H}_2\mathrm{O}. \qquad (2)$$

It follows that the overall reaction rate depends upon the ease of the oxidation of the trivalent ion and upon the ease of the reduction of the tetravalent ion. On a highly oxidized catalyst, it seems to depend predominantly upon the ease of the reduction, and on highly reduced catalyst, upon the ease of the oxidation.

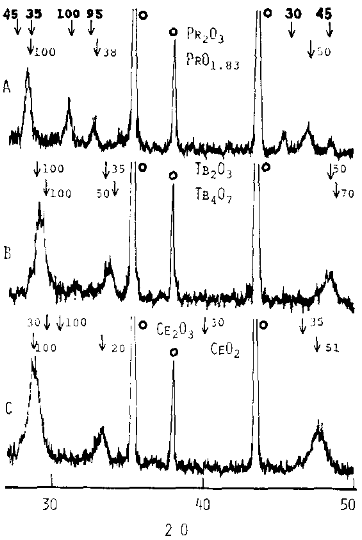

FIG. 8. X-Ray diffraction patterns of praseodymium (A), terbium (B), and cerium (C) oxides after the reaction. (○) diffraction lines of α-alumina; arrows and numerals, position and I/I_0 quoted from ASTM cards.

Figure 8 shows the X-ray diffraction patterns of praseodymium, terbium, and cerium oxides after the reaction. The composition of the usually obtained praseodymium oxide is commonly referred to as Pr_6O_{11} or Pr_4O_7. It requires the reduction of Pr_6O_{11} by hydrogen at 600°C to prepare the stoichiometric oxide Pr_2O_3, and the oxidation with atomic oxygen at 1400°C or with oxygen of 50 atm at 300°C to prepare PrO_2 (*2*). The X-ray diffraction pattern indicates that the used praseodymium oxide consists of not only Pr_6O_{11} but also Pr_2O_3. The composition of terbium oxide usually obtained is commonly given as Tb_4O_7. The preparation of the stoichiometric oxides requires the reduction or the oxidation under approximately the same conditions as to prepare the stoichiometric oxides of praseodymium (*2*). It is not obvious from the X-ray diffraction pattern that the used terbium oxide consists of either Tb_4O_7 or Tb_2O_3, because both oxides give the diffraction lines at almost the same positions. But it seems reasonable from analogy with praseodymium oxide to regard the used terbium oxide as the mixture of Tb_4O_7 and Tb_2O_3. The composition of the most stable cerium oxide is CeO_2, and it requires the reduction of CeO_2 by hydrogen at 1400°C to prepare Ce_2O_3 (*2*). Only the diffraction lines of CeO_2 could be observed in the X-ray diffraction pattern in Fig. 8. The color of the fresh catalyst and the used one cooled in a stream of the reaction mixture was pale yellow, but the catalyst under the reaction condition was blue. The color of cerium oxide varies with the oxidation state as shown in Table 2 (*18*). The α-phase is CeO_2 with little anion vacancies, and β-phase is $CeO_{1.812}$ derived from eight unit cells of the CeO_2 structure by the ordered omission of six O^{2-} ions. The color of cerium oxide under the reaction condition corresponds to that of $CeO_{1.902}$. For the other oxides, only the diffraction lines of the sesquioxides could be observed in the X-ray diffraction pattern, which is in good agreement with that the lanthanide sesquioxides cannot be reduced by hydrogen (*2*). After all, the catalysts can be regarded as considerably reduced under the reaction condition, which suggests that the catalytic activity mainly depends on the ease of the oxidation of the trivalent ion to the tetravalent one.

Such a hypothesis on the basis of the redox mechanism can explain a contradiction on the activity of cerium oxide in the literature. Table 3 shows the comparison of the activity of cerium oxide with

TABLE 2

Color and Phase of Cerium Oxide (*18*)

Composition	Color	Phase
CeO_2	Pale yellow	α
$CeO_{1.947}$	Gray-blue (light)	α, β
$CeO_{1.902}$	Gray-blue (medium)	α, β
$CeO_{1.883}$	Gray-blue (dark)	α, β

TABLE 3

Catalytic Activity of Cerium Oxide in Comparison with the Others

Reaction	Atm.	Activity	Ref.
O_2 IE[a]	Oxygen	Ce < Nd	(*5*)
CO oxidn.	$CO/O_2 = 1$	Ce < Nd	(*5*)
O_2 IE[a]	Oxygen	Ce < Pr	(*6*)
H_2 oxidn.	$H_2/O_2 = 2$	Ce < Pr	(*6*)
	$H_2/O_2 = 2$	Ce < Pr	(*7*)
C_3H_6 oxidn.	$C_3H_6/O_2 = 7/3$	Ce > Pr	(*6*)
C_4H_{10} oxidn.	$C_4H_{10}/O_2 = 1$	Ce > Pr	Present study

[a] Isotopic exchange of oxygen.

praseodymium oxide or neodymium oxide. In some reactions, the activity of cerium oxide is lower, and in the others, higher than that of praseodymium oxide or neodymium oxide. It may be reasonable, as a first approximation, that the oxidation state of the catalyst is determined by the ratio of the oxygen partial pressure to the stoichiometric pressure, though the reactant to be oxidized for each case is different. In the case where cerium oxide showed higher activity, cerium oxide seems significantly reduced, because the partial pressure of oxygen is only less than 16% of the stoichiometric pressure. The higher activity of cerium oxide may be attributed to the highest stability of the tetravalent cerium ion among the lanthanides, because the rate determining step on the reduced catalyst is the oxidation of the trivalent ion. In another case, the activity was measured under the atmosphere of oxygen or in excess of oxygen. Under such an atmosphere, cerium oxide is easily oxidized to CeO_2. The high stability of the tetravalent ion seems to result in the lower activity, because the reduction of the catalyst surface is the rate determining step on the oxidized catalyst.

As evident from the above discussion, it is reasonable to attribute the catalytic activity of the lanthanide oxides under the reducing atmosphere to the stability of the tetravalent ion relative to the trivalent ion. The heat of formation of the dioxide (LnO_2) from the sesquioxide ($LnO_{1.5}$) is one of the measures of the stability of the tetravalent ion relative to the trivalent ion in the oxide. The heat of formation of the dioxide and the sesquioxide can be given as follows from the Born-Haber cycle.

$$\Delta H_f^0(\mathrm{LnO_2}) = S + D + \sum^{4} I_i - 2E - U_2, \quad (3)$$

$$\Delta H_f^0(\mathrm{LnO_{1.5}}) = S + \tfrac{3}{4}D + \sum^{3} I_i - \tfrac{3}{2}E - U_{1.5}, \quad (4)$$

where S is the heat of vaporization of the lanthanides, I_i is the i-th ionization potential, D is the heat of dissociation of oxygen, E is the electron affinity of oxygen atom, and U_i is the lattice energy of LnO_i. The heat of formation of the dioxide from the sesquioxide, $\Delta(\Delta H_f^0)$, is given by the difference between the two.

$$\Delta(\Delta H_f^0) = I_4 - \Delta U_i + \tfrac{1}{4}D - \tfrac{1}{2}E, \quad (5)$$

where ΔU_i is the difference between U_2 and $U_{1.5}$. Only the tendency of the variation of $\Delta(\Delta H_f^0)$ with the atomic number can be represented by the fourth ionization potential, because the lattice energy increases monotonously as the interatomic distance decreases on going from lanthanum to lutetium (*19, 20*), and because the last two terms in Eq. (5) is constant for all the lanthanide oxides.

Figure 9 shows the fourth ionization potential of the lanthanides (*21*). The variation of the fourth ionization potential with the atomic number is in good agreement with that of the yield of carbon dioxide in Fig. 2. The first and the second maximums of the catalytic activity were observed on the oxides of cerium and terbium where the minimums of the fourth ionization potential are also observed. The catalytic activity decreased as the fourth ionization potential increases on going from cerium to gadolinium and from terbium to lutetium. The fourth ionization potential of lanthanum which has not been reported is expected to be significantly large (line in Fig. 9). Because it is difficult to remove one electron from the trivalent lanthanum ion with the electronic configuration of the closed Xe shell. If so, the large ionization potential of lanthanum is in good agreement with the significantly low activity of lanthanum oxide.

As shown in Fig. 10, a good correlation was obtained between the fourth ionization potential and the yield of carbon dioxide at 450°C, which suggests that the contribution of the term ΔU_i in Eq. (5) is small. The redox mechanism does not imply the oxidation and the reduction between the dioxide and the sesquioxide, but the oxidation and the reduction of the catalyst surface with the constant bulk structure. The heat of formation of the vacancy must be taken into consideration instead of the change of the lattice energy. Because the vacancy must be formed when the catalyst surface is successively oxidized and reduced with the constant bulk structure. The good correlation in Fig. 10, however, suggests that the contribution of the heat of formation of the vacancy is not so large, though it is obscure whether the small effect of the heat of formation of vacancy is peculiar to the lanthanide oxide or not.

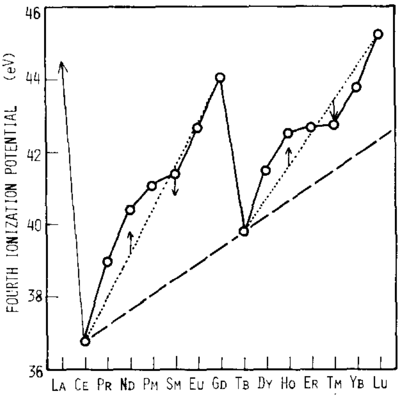

Fig. 9. Fourth ionization potential of lanthanide (*21*) (——), (— —), (····) and arrows represent theoretically expected dependence of the fourth ionization potential on the atomic number.

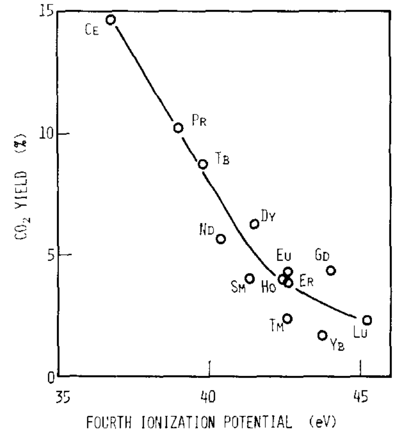

Fig. 10. Correlation between CO_2 yield at 450°C and the fourth ionization potential.

The Catalytic Activity and the Electronic Configuration

It is obvious from the above discussion that the catalytic activity depends on the electronic configuration of the inner $4f$ subshell which has little effect on the chemical property of the lanthanides. The discussion will hereinafter be made on the mechanism how the electronic configuration of the $4f$ subshell influences the catalytic activity of the lanthanide oxides, on referring to the good correlation between the catalytic activity and the fourth ionization potential of the lanthanides.

The dependence of the fourth ionization potential on the atomic number can be interpreted by applying Nelson's (*22*) interpretation of the third ionization potential of the $3d$ transition metals in the following way. The ionization potential is the difference in the energy between the $4f^n$ and the $4f^{n-1}$ subshells with the same positive charge of the closed Xe shell. The energy of the $4f$ subshell consists of the Coulomb attraction energy between the Xe shell and each $4f$ electron, U, and the interaction between the $4f$ electrons. The latter can be divided into the Coulomb repulsion energy and the exchange energy. The repulsion energy is approximately proportional to the number of the electron pairs, $\binom{n}{2}$, and the exchange energy, to the number of pairs of parallel spins, $m(n)$. Therefore, the energy of the $4f^n$ subshell is approximately given as follows.

$$E(n) = -n \cdot U + J \cdot \binom{n}{2} - K \cdot m(n), \quad (6)$$

where J and K are the proportionality constants. The negative signs of the first and the last terms are due to the fact that both the Coulomb attraction force and the exchange interaction stabilize the $4f$ electron. The ionization energy can be given by the difference between $E(n-1)$ and $E(n)$.

$$I = U - J \cdot (n-1) + K \cdot \Delta m, \quad (7)$$

where Δm is the change of the number of pairs of parallel spins accompanying the removal of one electron from the $4f^n$ subshell and is equal to $m(n) - m(n-1)$. The first term increases monotonously with the atomic number, because the positive charge of the closed Xe shell increases monotonously and the ionic radius decreases monotonously. Although the second term decreases with an increase in the atomic number, the increase in the first term seems predominant, and the sum of the first two terms, maybe, increases monotonously as shown by the broken line in Fig. 9. The last term shows a saw-toothed dependence on the atomic number. The trivalent cerium ion has one $4f$ electron with the spin quantum number, m_s, of $+\frac{1}{2}$, but no one with m_s of $-\frac{1}{2}$. The succeeding six trivalent ions successively add six $4f$ electrons with m_s of $+\frac{1}{2}$, but the number of the electrons with m_s of $-\frac{1}{2}$ remains zero. The tetravalent ions have one less electron than the corresponding trivalent ions. Therefore, $m(n)$ of the trivalent ion is equal to $\binom{n}{2}$ and Δm from the trivalent ion to the tetravalent ion is equal to $n - 1$, when n is the number of the $4f$ electron in the trivalent ion. The trivalent ions between terbium and lutetium have seven $4f$ electrons with m_s of $+\frac{1}{2}$ and $n - 7$ electrons with m_s of $-\frac{1}{2}$. The tetravalent ions have also seven electrons with m_s of $+\frac{1}{2}$ but $n - 8$ electrons with m_s of $-\frac{1}{2}$. Therefore, $m(n) = \binom{7}{2} + \binom{n-7}{2}$ and $\Delta m = n - 8$. After all, the last term is zero at cerium ($n = 1$) and terbium ($n = 8$), and increases linearly with the atomic number from cerium to gadolinium and from terbium to lutetium. The dotted line in Fig. 9 thus obtained from Eq. (7) is roughly in agreement with the dependence of the fourth ionization potential. Some irregularities may be attributed to a stabilization of the ion with the large total angular momentum quantum number (*19*), which is shown by arrows in Fig. 9.

The good correlation has been obtained between the catalytic activity of the lanthanide oxides and the fourth ionization potential, which can be explained by assuming that the rate determining step is the oxidation of the trivalent ion to the tetravalent ion. Further, the dependence of the fourth ionization potential on the atomic number has been related to the electronic configuration of the inner $4f$ subshell. Therefore, it is now possible to relate the dependence of the catalytic activity on the atomic number to the electronic configuration. The highest activity of cerium oxide corresponds to the facts that the Coulomb attraction between the closed Xe shell and each $4f$ electron is less than the succeeding lanthanide ions and that the tetravalent ion has the same exchange energy between the $4f$ electrons as the trivalent ion. The former is due to the smaller positive charge of the Xe shell and to the larger ionic radius than the others. And the latter is due to the fact that the trivalent cerium ion has only one electron in the 4*f* subshell. Both the Coulomb attraction energy and the exchange energy stabilize the 4*f* electrons and increase the energy necessary for the oxidation of the trivalent ion to the tetravalent ion, which is the rate determining step of the catalytic oxidation under the reducing atmosphere. The second highest activity of terbium oxide corresponds to the fact that the change of the exchange energy accompanying the oxidation of the trivalent ion to the tetravalent ion is zero just as cerium ion, though the Coulomb attraction energy is larger than cerium ion. The former is due to the fact that the trivalent terbium ion has only one electron with m_s of $-\frac{1}{2}$, though the number of the total 4*f* electrons is eight. The catalytic activity decreased as the atomic number increases on going from cerium to gadolinium and from terbium to lutetium. Such a decrease in the catalytic activity corresponds to the increases in the Coulomb attraction energy and in the change of the exchange energy. The increase in the Coulomb attraction energy is due to the increase in the positive charge of the closed Xe shell and to the decrease in the ionic radius. The increase in the change of the exchange energy is due to the increase in the 4*f* electrons with m_s of $+\frac{1}{2}$ or with m_s of $-\frac{1}{2}$. Significantly low activity of lanthanum oxide corresponds to the large energy required to oxidize the trivalent lanthanum ion which has the electronic configuration of the closed Xe shell. In addition, some irregularities in the catalytic activity may be expected from the stabilization of the ion with the large total orbital angular momentum quantum number. But such irregularities are not obvious within the accuracy of the experiment.

CONCLUSION

In the oxidation of butane on a series of lanthanide oxides, a good correlation has been obtained between the catalytic activity of the lanthanide oxides and the fourth ionization potential of the lanthanide elements, which can be interpreted well by assuming the rate determining step is the oxidation of the trivalent ion to the tetravalent ion.

The dependence of the catalytic activity on the atomic number has been interpreted by the following two factors based on the electronic configuration of the inner 4*f* subshell: the Coulomb attraction energy between the closed Xe shell and each 4*f* electron, and the change of the exchange energy between the 4*f* electrons accompanying the oxidation of the trivalent ion. The increase in both factors results in an increase in the energy required to oxidize the trivalent ion.

The highest activity of cerium oxide is due to the least Coulomb attraction energy and to the change of the exchange energy being zero. The second highest activity of terbium oxide is due to the fact that the latter is also zero but the former is larger than cerium ion. The decrease in the activity as the atomic number increases on going from cerium to gadolinium and from terbium to lutetium is due to the increase in both factors. The significantly low activity of lanthanum oxide is due to the large energy required to oxidize the trivalent lanthanum ion with the electronic configuration of the closed Xe shell.

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