JOURNAL OF CATALYSIS 93, 186–191 (1985)

Effect of Sm on the Catalytic Activity of Co_3O_4 in the Oxidation of Toluene

A considerable attention has been paid to the development of nonprecious metal combustion catalysts. Although transition metal oxides of the first series are used as combustion catalysts (*1*), their activity is relatively low. Therefore, second components are used as co-catalysts in order to improve their activity. The rare earth metals are known as effective additives. The best known catalyst systems, in which rare earth metals are combined with various transition metals, are the perovskite-type compounds. These include $LaFe_{1-x}M_xO_3$ (M = Cr, Mn, Co, Ni) (*2*), $La_{1-x}Sr_xCoO_3$ (*3*), $LaMn_{1-x}Cu_xO_{3-x}$ (*4*), $LaCoO_3$ (*5*), and $Ln_{1-x}Pb_xMnO_3$ (Ln = La, Pr, Nd) (*6*). The behavior of single-component rare earth oxides has also been investigated in connection with the reactivity of their lattice oxygen atoms (*7, 8*).

The catalytic activity of the cobalt–samarium (Sm) system, however, has not been investigated in detail (*9*). Moreover, the amount of lanthanoids incorporated in the perovskite-type catalysts is, in all cases, large, amounting to 40–100% of the partner transition metals. The effect of an addition of small amount of lanthanoids to the transition metal oxides has not been studied extensively.

This paper deals with the effect of the addition of small amount of lanthanoids on the catalytic activity of cobalt oxide in the oxidation of toluene, particular attention being given to the effect of Sm.

The composite oxides of Co and lanthanoids (Ln) were prepared by coprecipitation from a mixed aqueous solution of cobalt(II) nitrate and lanthanoid nitrate. The resultant precipitate was washed with a 500-ml portion of water five times, and then dried in air at 100°C. The dry precipitate was molded into a bar (0.5 × 1 × 5 cm), and calcined at a prescribed temperature for 2 h in air. The catalysts were stored under a nitrogen atmosphere and were cut into about 20-mesh size before use. As $Co(OH)_2$ changed into Co_3O_4 upon heating to 265°C, cobalt oxide without lanthanoids prepared in this work was designated as Co_3O_4 (*10*).

Reactions were carried out using an ordinary flow reactor under atmospheric pressure. Details of the reactor and the procedure were described in the previous paper (*11*). One milliliter of the catalysts was used and the concentration of toluene entering the reactor was 1400 ppm. Air was used as an oxidizing gas and its space velocity was 21,400 h^{-1}. The temperature of the catalyst bed was raised from room temperature at a constant rate of 3.75°C/min by an electric furnace. The temperature of the initiation of oxidation (T_1), the temperature where the concentration of CO_2 at the outlet of the reactor exceeded 300 ppm, and of apparently complete oxidation (T_2) where conversion to CO_2 reached 100% based upon toluene fed into the reactor were observed. In most cases, the temperature of the catalyst bed rose spontaneously due to the accumulation of the heat of reaction after T_1 was reached. Simultaneously, toluene conversion to CO_2 increased suddenly and, in some cases, it exceeded 100% due to the combustion of the carbonaceous deposit on the surface of the catalysts; this phenomenon is called "light off" (*1*). It was, therefore, difficult to determine T_2 accurately, and the following procedure was used to define T_2. After light off had occurred, the

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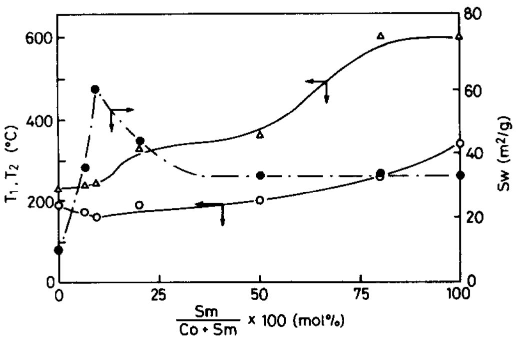

FIG. 1. Effect of the composition of Co/Sm calcined at 500°C. [Toluene] = 1400 ppm, $SV = 21400\ h^{-1}$, T_1 (○), T_2 (△), and BET surface area (⊙).

temperature of the catalyst bed was allowed to decrease rapidly, and, then, it was again increased at a rate of 3.75°C/min, allowing relatively mild onset of oxidation to occur, although slight light off was observed again in some cases. After approximately 100% conversion to CO_2 had been attained, no increase in CO_2 yield was confirmed by the further increase in the temperature of the catalyst bed. Then the temperature of the catalyst bed was gradually decreased, as the yield of CO_2 was monitored. The T_2 was defined as the temperature at which the CO_2 concentration began to decrease during the above process. The T_2 was determined within 30 min following the occurrence of light off. Although trace amount of toluene which escaped oxidation was detected during the reaction, even at T_2 in some case, no other reaction products (e.g., formaldehyde, formic acid, methanol, or acetic acid) were detected. Despite the lack of strictly complete oxidation at T_2, this temperature was employed as a measure of the activity of the catalysts. The reaction scarcely proceeded in the absence of the catalysts; CO_2 yields at 400 and 600°C were 4.0 and 7.1% based upon toluene fed, respectively.

The reduction and oxidation of the catalysts were carried out at 575°C by passing H_2–He mixture (60 ml/min, $H_2 = 5\%$) over the oxide catalysts and O_2–He mixture (60 ml/min, $O_2 = 5\%$) over the reduced catalysts in the sample chamber of a thermobalance, respectively. The temperature of the catalyst rose from 575 to 590°C at an early stage of the oxidation due to the rapid reaction of oxygen with the reduced catalyst, and then gradually decreased to 575°C.

Oxidation of toluene was carried out using various Co/*Ln* systems (*Ln* = La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er) with a molar ratio of Co to *Ln* of 16.7 [Co/*Ln* (10/0.6)] calcined at 500°C. Both T_1 and T_2 differed remarkably according to the type of *Ln* employed. From the comparison of T_2's, it was found that Co/Ce (240°C), Co/Sm (240°C), Co/Dy (235°C), and Co/Er (240°C) were comparatively active. As Co/Sm showed the lowest T_1(175°C) among these composite oxides (Co/Ce: 230°C, Co/Dy: 195°C, Co/Er: 190°C), the catalytic activity of Co/Sm was investigated hereafter.

Figure 1 shows the effect of the composition of Co/Sm catalysts on their catalytic activity in the oxidation of toluene, all catalysts having been calcined at 500°C. The catalysts with less than 10 mol% of Sm had the same activity as Co_3O_4; however, further addition of Sm decreased the activity monotonically. The BET surface area of the catalysts increased remarkably with the addition of rather small amount of Sm. As an addition of a large amount of Sm had detrimental effect, the quantity of Sm added was kept small (molar ratio of Co to Sm: 10/0.6).

Figure 2 shows the effect of the calcination temperature of Co/Sm (10/0.6) and Co_3O_4 on their catalytic activity. Although T_1 for Co_3O_4 did not differ much with the change of calcination temperature, the T_2 rose remarkably with an increase in calcination temperature above 650°C. In the case of Co/Sm, however, the activity remained almost constant for the catalyst calcined at a temperature up to 800°C. As combustion catalysts often suffer high-temperature reactions, they must be prepared at relatively high calcination temperatures. The result shown in Fig. 2 indicates that an addition of Sm is effective for improving

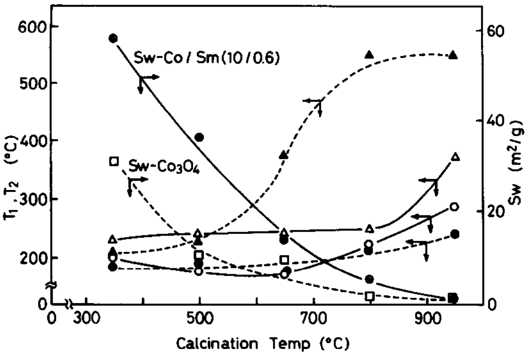

FIG. 2. Effect of the calcination temperature of Co_3O_4 and Co/Sm (10/0.6). [Toluene] = 1400 ppm, *SV* = 21400 h^{-1}; T_1 (○) and T_2 (△) for Co/Sm (10/0.6), T_1 (●) and T_2 (▲) for Co_3O_4.

the catalytic activity of Co_3O_4 prepared at high temperatures. The change of the BET surface areas of the catalysts with the change of calcination temperature is also shown in the figure. The surface area of Co/Sm was always larger than that of Co_3O_4. The increase in surface area on addition of Sm, however, is not the only cause for the higher activity of Co/Sm calcined above 650°C, because the activity of Co/Sm calcined at 950°C was also higher than that of Co_3O_4 calcined at the same temperature, despite the fact that their surface areas were almost the same.

The X-ray diffraction analysis of Co_3O_4 and Co/Sm (10/0.6) prepared at 500, 650, and 800°C showed that an addition of Sm decreased the crystallinity of Co_3O_4. The retardation in crystallization of Co/Sm was also shown by scanning electron microscope (SEM). Figure 3 shows the SEM photographs of Co_3O_4 and Co/Sm (10/0.6), both prepared at 800°C. The particle size of Co/Sm was much smaller than that of Co_3O_4, which is in accord with the larger surface area of the former.

As the activity of Co/Sm (10/0.6) calcined at high temperature (>650°C) was much higher than that of Co_3O_4 calcined at the same temperature, we also investigated the effect of the composition of Co/Sm catalysts calcined at 800°C (Table 1). The comparison of the values of T_2 shows that the Co/Sm system containing as high as 80% of Sm has almost the same activity as Co_3O_4, although Sm is not considered an active combustion catalyst. Some Co/*Ln* perovskite-type compounds are known as active combustion catalysts (*2, 3, 5, 6*). The X-ray diffraction analysis of Co/Sm catalysts listed in Table 1 indicated the presence of perovskite-type composite oxide of Co/Sm in all cases. As Co/Sm (1/1), which was mainly composed of perovskite-type Co/Sm, was more active than Co_3O_4, it is seen that perovskite-type Co/Sm is an effective combustion catalyst. The Co/Sm (10/0.6), however, had much higher activity than Co/Sm (1/1), indicating that the effect of an addition of Sm to Co is not solely due to the formation of the perovskite-type compound.

The Co_3O_4 and Co/Sm (10/0.6), both calcined at 800°C, were used in the reaction at high temperatures, and the change in their activity was investigated (Fig. 4). The temperature of the catalyst bed was raised to 700, 800, or 850°C at a rate of 3.75°C/min, and then the reaction was stopped or was continued at these temperatures for 2 h. The T_2's determined in this experiment were higher than those obtained in the previous experiments shown, for example, in Fig. 2, because the temperature of the catalyst bed was not lowered gradually after ap-

TABLE 1

Effect of the Composition of Co/Sm Calcined at 800°C[a]

Sm (mol%)	T_1 (°C)	T_2 (°C)	*Sw* (m^2/g)
0	225	550	1.4
5.7	225	245	5.4
9.1	215	310	3.0
20	230	350	2.4
50	240	450	3.0
80	265	530	7.3
100	270	—	12.3

[a] Reaction condition: [Toluene] = 1400 ppm, *SV* = 21,400 h^{-1}.

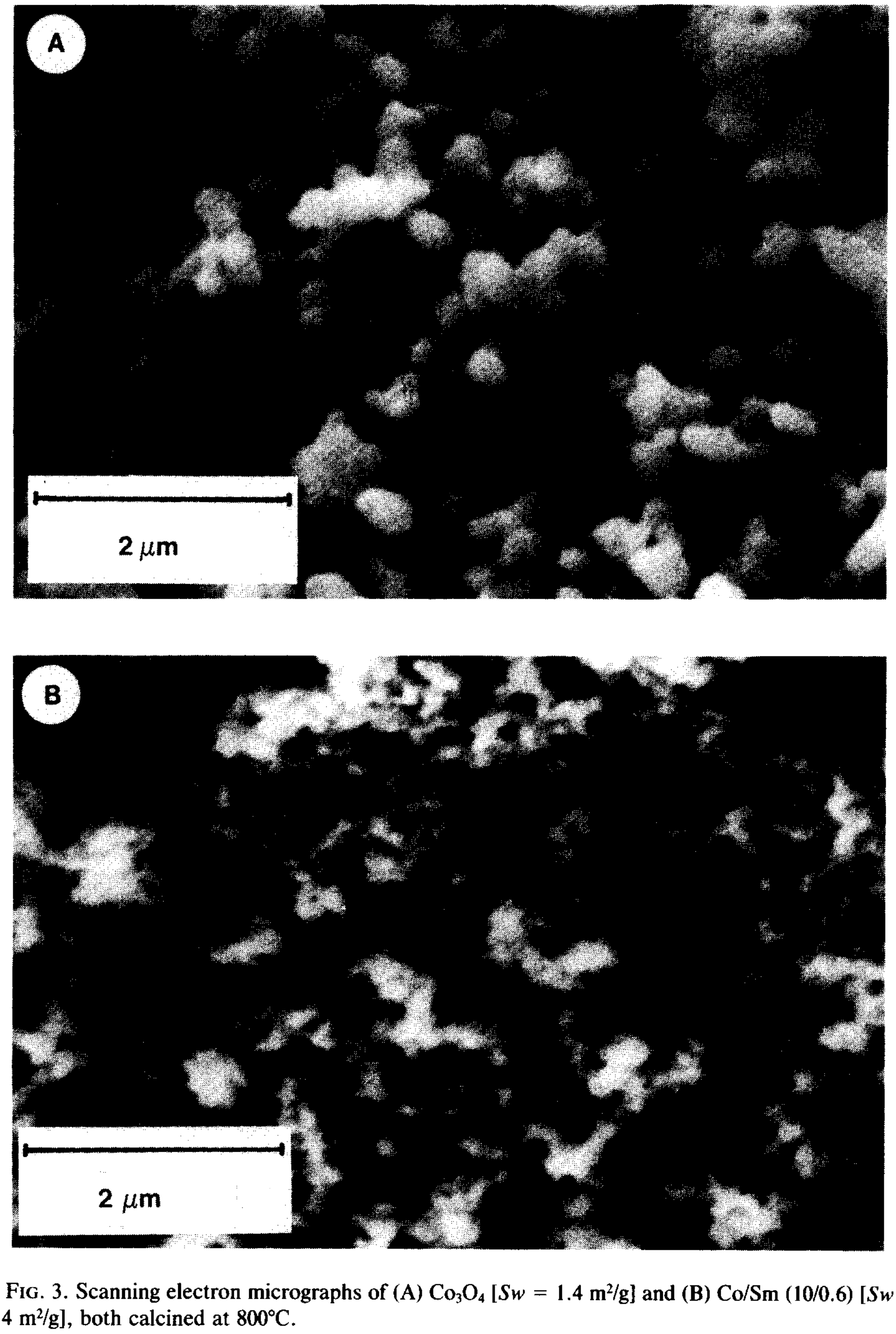

FIG. 3. Scanning electron micrographs of (A) Co_3O_4 [*Sw* = 1.4 m^2/g] and (B) Co/Sm (10/0.6) [*Sw* = 5.4 m^2/g], both calcined at 800°C.

proximately 100% conversion to CO_2 was obtained. Therefore, the values of T_2 shown in Fig. 4 are inaccurate and should be regarded as a rough measure of the activity of the catalysts. The T_1 for Co/Sm (10/0.6) was scarcely affected by the treatment at high temperatures, and T_2 rose gradually from 305°C for fresh catalyst to 355°C after the fifth treatment. In the case of Co_3O_4, however, deactivation was more remarkable.

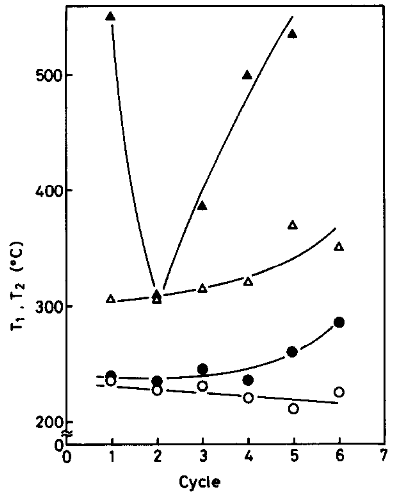

FIG. 4. Durability of Co_3O_4 and Co/Sm (10/0.6), both prepared at 800°C, in high-temperature reactions. [Toluene] = 1400 ppm, SV = 21400 h^{-1}, Sw = 1.4 m^2/g [Co_3O_4] and 5.4 m^2/g [Co/Sm (10/0.6)]; T_1 (○) and T_2 (△) for Co/Sm (10/0.6), T_1 (●) and T_2 (▲) for Co_3O_4. Cycles 1 and 2: temperature of the catalyst bed was raised to 700°C and then kept constant for 2 h. Cycles 3 and 5: temperature was raised to 850°C and then kept constant for 2 h. Cycles 4 and 6: temperature was raised to 850°C and then the reaction was stopped.

The T_1 after the fifth treatment (275°C) was higher than that for the fresh catalyst (240°C). Although T_2 was lowered after the first treatment, it rose again after the second treatment and complete oxidation of toluene could not be attained at the sixth cycle; conversion to CO_2 was 87.5% at 850°C. Although the increase in the activity of Co_3O_4 after the first treatment could not be explained, the increase in the activity followed by a remarkable deactivation suggests that the state of Co_3O_4 changes more easily in the reaction at high temperature than that of the Co/Sm catalyst. The Sm is, therefore, effective in improving the thermal stability of Co_3O_4. No difference between the fresh states and the states after the sixth heat treatment of both catalysts was observed by X-ray diffraction analysis and SEM method, except for the slight change in BET surface area of Co/Sm (10/0.6); the BET surface area of Co/Sm (10/0.6) decreased from 5.4 to 4.2 m^2/g, while that of Co_3O_4 (1.4 m^2/g) did not change by the heat treatments.

The Co_3O_4 and Co/Sm (10/0.6), both calcined at 800°C, were reduced by hydrogen followed by oxidation with oxygen at 575°C in the sample chamber of the thermobalance, and the behavior of the catalysts, as measured by their weight change due to the desorption and adsorption of their lattice oxygen, was investigated. The reduction–oxidation cycle was repeated four times. The reduction of Co/Sm (10/0.6) was carried out up to 100% removal of its lattice oxygen. In the case of Co_3O_4, however, complete reduction was not achieved (90–97%) because it took a long time to reduce it completely due to the inertness of the lattice oxygen at high degree of reduction. The change of the maximum rates of reduction and oxidation is shown in Fig. 5. The desorption of the lattice oxygen and adsorption of oxygen from the vapor phase took place easily for Co/Sm (10/0.6). Although both rates increased slightly with the oxidation–reduction cycles, the increase was not remarkable. Although rate

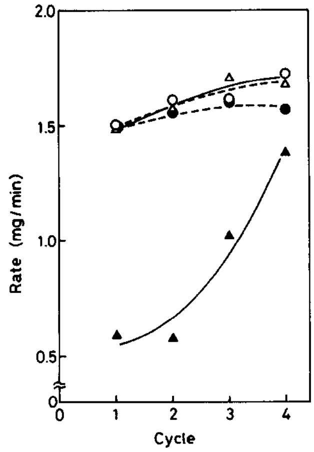

FIG. 5. Rates of reduction [Co/Sm (10/0.6) (△), Co_3O_4 (▲)] and oxidation [Co/Sm (10/0.6) (○), Co_3O_4 (●)]. The catalysts (25 mg) were prepared at 800°C. Sw = 3.7 m^2/g [Co_3O_4] and 9.6 m^2/g [Co/Sm (10/0.6)], (He + O_2) = (He + H_2) = 60 ml/min, [O_2] = [H_2] = 5 vol%. Reduction and oxidation temps. = 575°C. Rates are expressed by the weight loss and gain of the catalysts per minute.

of oxidation increased only slightly in the case of Co_3O_4, its rate of reduction increased remarkably with the repetition of oxidation–reduction cycles. During the oxidation of hydrocarbons over metal catalysts, the surfaces of the catalysts continuously suffer oxidation–reduction cycles by the hydrocarbons and oxygen, which is similar to the treatment shown in Fig. 5 although the oxidation–reduction amplitude is not so large (*12*). The results shown in Fig. 5 indicate that the state of Co_3O_4 changes more easily than that of Co/Sm (10/0.6) during the reaction, which may be the cause of the increase in its activity in the early stage of the treatment at high temperature followed by a remarkable deactivation (Fig. 4). Even in the fourth cycle, however, the rate of the reduction of Co_3O_4 was smaller than that of Co/Sm (10/0.6). As the diffusion of hydrogen or oxygen will take part in the reduction–oxidation of the catalysts, the result shown in Fig. 5 is qualitative. However, it is clear that the lattice oxygen of Co/Sm (10/0.6) is more readily desorbed than that of Co_3O_4, which will be the cause of the higher activity of Co/Sm (10/0.6) in the oxidation of toluene.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of this work by a grant from Tanigawa Netsugijutsu Shinko Kikin. They also express their gratitude to Professor T. Nishikawa of Kyoto Institute of Technology for his continuous encouragement and to Mr. K. Utani and Mr. H. Matsushige for their assistance in carrying out this work.

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Received July 14, 1983

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