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Pronounced Catalytic Activity of $La_{1-x}Sr_xCoO_3$ Highly Dispersed on ZrO_2 for Complete Oxidation of Propane

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$LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ highly dispersed on ZrO_2 was prepared by impregnation method. The high dispersion was confirmed by IR spectra of pyridine adsorbed on ZrO_2 as well as by TEM and XRD. The catalysts showed very high catalytic activities for the complete oxidation of propane.

The support effect is important when mixed oxides are synthesized as thin layers or fine particles on the surface of metal oxide supports. We recently reported that $La_{0.8}Sr_{0.2}CoO_3$ was formed on cordierite when its surface was precoated with La_2O_3.[1)] However, the surface area of cordierite is low. So, we attempted to synthesize perovskite-type mixed oxides ($La_{1-x}Sr_xCoO_3$; $x = 0, 0.2$) on the surface of various oxides, in order to increase the surface area and improve the catalytic activity, and found that ZrO_2 was excellent as the support.

Metal oxides used as the supports were commercially obtained as oxides (Gd_2O_3, Sm_2O_3, La_2O_3, Nd_2O_3, Al_2O_3, and SiO_2) or prepared from acetates (SrO, BaO, CeO_2, ZrO_2, and TiO_2). These oxides and acetates were calcined at 850 °C for 5 h in air before use. The formation of each oxide was confirmed by X-ray diffraction (XRD) patterns. These supports were impregnated with aqueous solutions of mixtures of La, Sr, and Co acetates by an incipient wetness method. For high levels of loading, the impregnation-drying cycle was repeated several times. After final drying at about 100 °C they were calcined at 850 °C for 5 h in air. The catalytic oxidation of propane was carried out at 227 - 400 °C with a flow system, after the catalysts (about 0.1 g) were pretreated at 450 °C in an O_2 stream. Complete oxidation was the only reaction observed. The feed gas was a gas mixture of propane (0.83%), O_2 (33.3%), and N_2 (balance).

The surface areas of the supports and the rates of catalytic oxidation of propane over $La_{0.8}Sr_{0.2}CoO_3$ at 400 °C are summarized in Fig. 1, where the rates are normalized to unit weight of supported perovskite. Here, the expressions like $La_{0.8}Sr_{0.2}CoO_3$ and perovskite indicate only the composition and do not necessarily mean that the perovskite structure was actually formed. It is noted that the rate varied greatly with the kind of oxide carriers. Most oxides loaded with $La_{0.8}Sr_{0.2}CoO_3$ showed very low activities, but high catalytic activity exceeding the $La_{0.8}Sr_{0.2}CoO_3$ bulk was obtained when ZrO_2 or CeO_2 was used. We

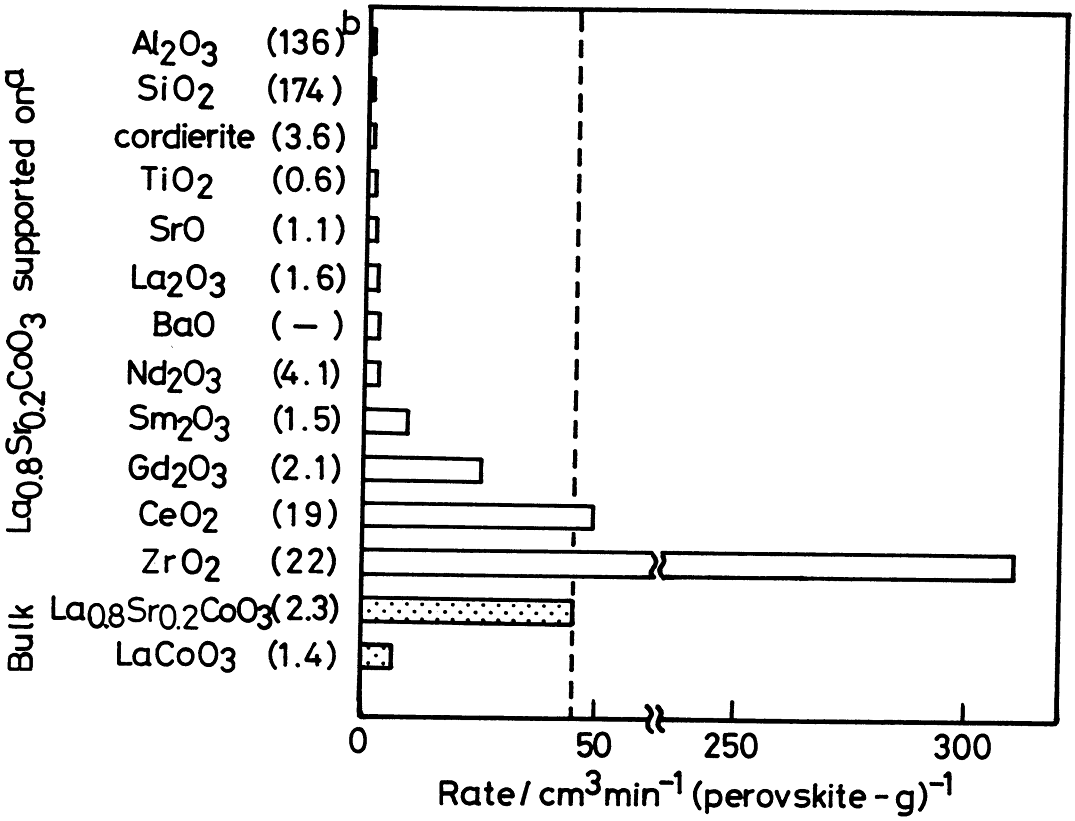

Fig. 1. Catalytic activities of perovskites supported on various oxides for oxidation of propane at 400 °C.

a) The amount of $La_{0.8}Sr_{0.2}CoO_3$ loaded was 5.8 wt%.

b) Surface areas of the supports ($m^2 g^{-1}$) are given in parentheses.

previously obtained a high catalytic activity by using La_2O_3-precoated cordierite as the support,$^{1)}$ but the activity of this catalyst normalized to the weight of $La_{0.8}Sr_{0.2}CoO_3$ was still slightly lower than the $La_{0.8}Sr_{0.2}CoO_3$ bulk itself. Therefore, the very high activity of ZrO_2-loaded one is worthy of note.

The effects of varying the amount of perovskite loaded were examined in the cases of $La_{0.8}Sr_{0.2}CoO_3$ and $LaCoO_3$. The latter was slightly more active, although the reason is not clear at present. So the results for $LaCoO_3$ are shown in Fig. 2. The rate increased at first linearly with the increasing amount of $LaCoO_3$, and then gradually decreased showing a maximum at ca. 5 wt%. Two lots of ZrO_2 having different surface areas (26 and 15 $m^2 g^{-1}$) apparently behaved similarly. The loading level of 5 wt% is of the order of monolayer coverage of $LaCoO_3$ on ZrO_2.$^{2)}$ Results for $La_{0.8}Sr_{0.2}CoO_3$ were similar, a maximum being at ca. 4 wt%. In the XRD measurements applied for $LaCoO_3$, no phases other than monoclinic ZrO_2 were detected up to the loading level of 5.1 wt% and weak lines due to the perovskite structure appeared at 2θ (CuKα) = 32.8 ° and 33.1 ° for the 7.5 wt% loading. This result suggests that "$LaCoO_3$" was highly dispersed as fine particles or thin layers on the surface of ZrO_2 up to the loading level of about 5 wt%.

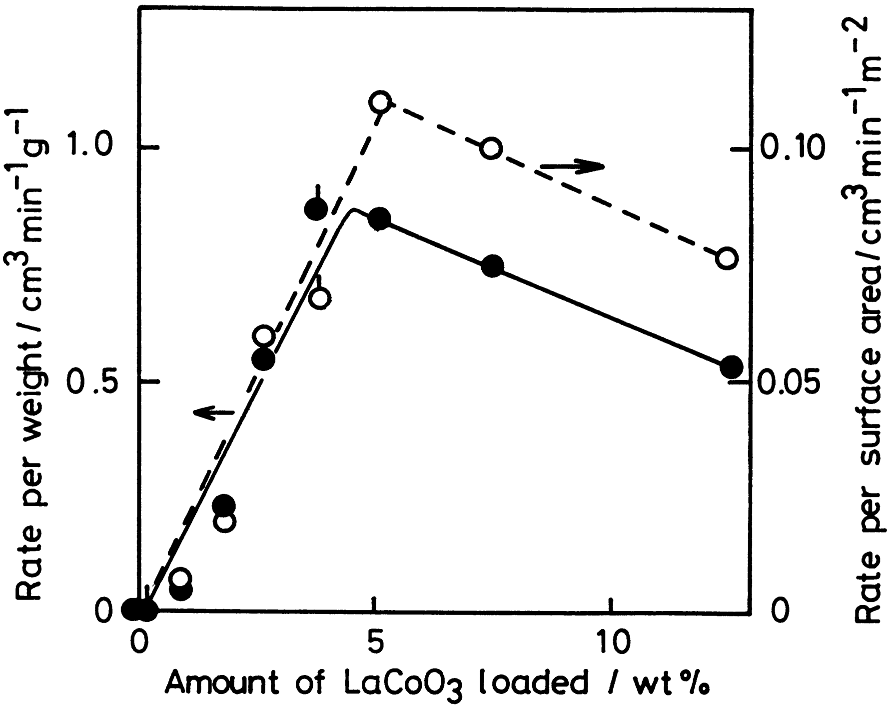

Fig. 2. Effects of the amount of $LaCoO_3$ loaded on ZrO_2 on the rates of oxidation of propane at 275 °C.
Flags indicate ZrO_2 having the surface area of 26 m^2g^{-1}. ZrO_2 with 15 m^2g^{-1} were used for the others.

To confirm the above idea, the surfaces of the catalysts were examined by IR spectra of adsorbed pyridine. After the sample was evacuated at 400 °C, it was exposed to pyridine vapor at room temperature and then evacuated at 130 °C. The bands at 1446 (strong), 1608 (strong), 1488 (weak), and 1574 (weak) cm^{-1} were observed in the range of 1400 - 1700 cm^{-1}. The band positions coincide with those observed for pyridine coordinated with Zr^{4+} on the surface of ZrO_2.$^{3)}$ As shown in Fig. 3, the intensity of the IR band at 1446 cm^{-1} decreased with the amount of $LaCoO_3$ loaded and the band almost disappeared at 5.1 wt% and above. The band at 1608 cm^{-1} varied in the same manner. The surface area also decreased, but the variation of the IR band intensity was much greater, so that the above trend was essentially the same when the intensities were normalized to the weight of catalysts. This result shows that when the loading level of $LaCoO_3$ was increased the surface of ZrO_2 was covered to an increasing extent by a substance inactive to pyridine chemisorption. The structure of this substance is not known at present, but it is probably a perovskite or the like, since the perovskite structure was detectable by XRD when the loading amount was increased to 7.5 wt%. Hence, it may be concluded that $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$ or the like was formed in highly dispersed states on the surface of ZrO_2 up to a certain level of loading, and that this high dispersion is the prime reason of the high catalytic activity. It has been reported that perovskites are good electrode materials when ZrO_2 is used as solid electrolyte.[4] Probably, the structure of the perovskites fits geometrically and chemically the surface of ZrO_2. In accordance with this idea, the TEM observation did not detect any segregated particles of perovskite below the 5.1 wt% loading.

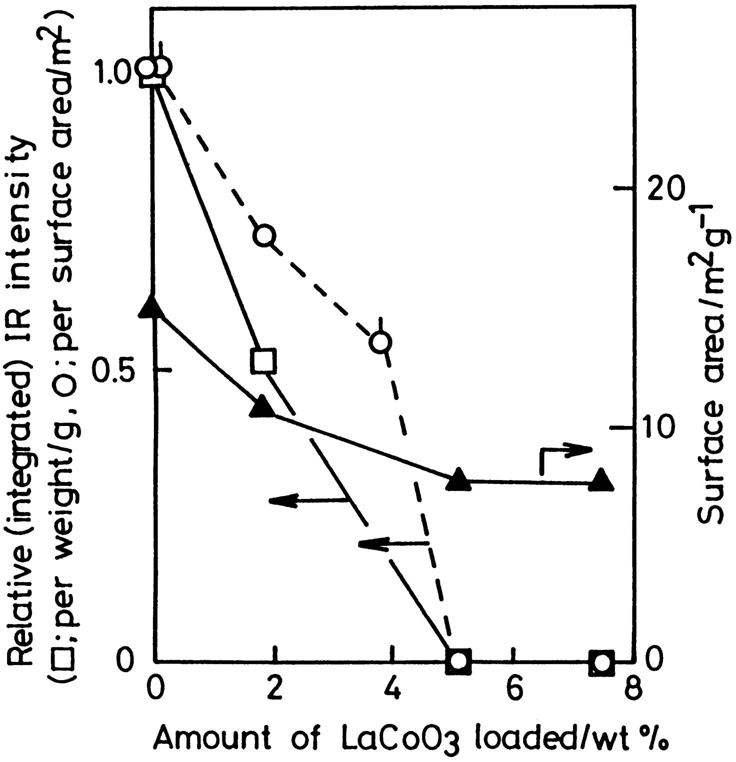

Fig. 3. Change in relative integrated IR peak intensity (1446 cm^{-1}) and surface area with the amount of $LaCoO_3$ loaded. Flags attached indicate those as explained in Fig. 2.

Part of the present letter has been preliminarily presented.[5]

The authors thank Mr. Tsunakawa for TEM measurements.

References

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2) Monolayer of La^{3+} + 3 O^{2-} ions on the surface of ZrO_2 having the surface area of 26 m^2g^{-1} corresponds to 4.8 wt% loading of $LaCoO_3$. If one assumes, for example, a thin layer of 2.5 Å (double layers of O^{2-}), the coverage at this loading level becomes 0.5.

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