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Unique Catalytic Activity of Platinum Eluted into Perovskite in the Solid Phase

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Abstract It has been found that Pt eluted into the $(La_{0.7}Sr_{0.2}Ba_{0.1})ScO_{3-\delta}$ perovskite oxide exhibited higher catalytic activity for CO oxidation than for H_2 oxidation under separate reaction conditions, a behaviour which differs from that of conventional Pt catalysts. The unique activity appeared when ionic Pt in the perovskite lattice was partly reduced, forming Pt nanoparticles on the surface.

Keywords Platinum · Oxidation catalyst · Carbon monoxide · Hydrogen · Perovskite · Oxide support

1 Introduction

Catalytic oxidation of CO and H_2 has been intensively studied owing to the industrial demand for the removal of residual CO from H_2 sources for fuel cells [1, 2]. Most noble metals, except for Au, intrinsically exhibit higher activity for H_2 oxidation than for CO oxidation, which is mainly explained by the strong adsorption of CO on the noble metals [3, 4]. We have recently reported the solid-phase elution (SE) of Pt into perovskite oxide [5]. In this communication, we report that Pt deposited on perovskite by the newly developed SE method shows the opposite catalytic performance, that is, higher activity for CO oxidation than for H_2 oxidation.

2 Experimental

Preparation of $(La_{0.7}Sr_{0.2}Ba_{0.1})ScO_{3-\delta}$ (LSBS, surface area: 3 m^2/g) and the solid-phase elution of Pt have been described in detail elsewhere [5]. In the deposition-precipitation (DP) method, $H_2PtCl_6 \cdot 6H_2O$ was used as a starting material, and the catalyst samples were calcined at 673 K for 4 h in air [6]. Catalytic activities were measured using a fixed-bed flow reactor with a space velocity of 20,000 ml/h/g-cat. Reactant gas for the separate oxidations was 1 vol % CO or H_2 in air, whereas a mixture of $H_2/CO/O_2 =$ 96/2/2 vol % was fed for the preferential oxidation of CO in the presence of excess H_2 (PROX). The effluent gas was analyzed with a gas chromatograph equipped with a thermal conductivity detector. Prior to the first measurements after calcination, the catalyst samples were reduced at 623 K for 1 h in 20 vol % H_2 (Ar balance). For the repeated measurements, the samples were refreshed by heating at 423 K for 0.5 h in air.

3 Results and Discussion

Figure 1a and b show a drastic change in the colour of LSBS perovskite powder, from light yellow before to ultramarine blue after calcination over Pt foil at 1898 K for 10 h in air. Incorporation of Pt into perovskite was confirmed by inductively coupled plasma (ICP) optical emission spectroscopy. The molar composition of Pt/LSBS determined by ICP was La:Sr:Ba:Sc:Pt = 0.70:0.20:0.09:0.95:0.006, corresponding to 0.5 wt % Pt/LSBS. When the blue

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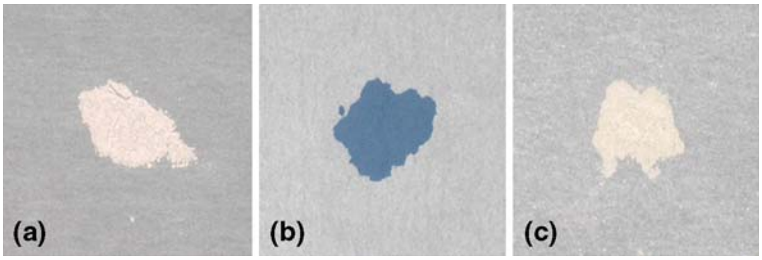

Fig. 1 Appearance of the (**a**) LSBS perovskite powder, (**b**) LSBS calcined over Pt foil at 1898 K for 10 h (Pt/LSBS-SE), and (**c**) Pt/LSBS-SE after reduction under the flow of 20 vol % H_2 in Ar at 553 K for 1 h

powder sample was pretreated by heating under an air flow, no activity was observed for CO oxidation, and a trace amount of H_2 was oxidised at high temperatures (data not shown). After the sample was reduced by H_2 at temperatures higher than 550 K, the sample colour changed to light greyish yellow, as shown in Fig. 1c, and CO oxidation started at 425 K (Fig. 2a). CO conversion jumped at ~490 K to full, which suggests local heat accumulation caused by an exothermic reaction burst. When the reaction temperature decreased, the activity dropped at ~480 K. Heating and cooling conversion curves were well reproduced in repeated measurements. In contrast, just after the H_2 reduction, the sample showed only slight activity for H_2 oxidation above 500 K ("H_2 1st" in Fig. 2a). It is interesting that the H_2 oxidation activity increased after CO oxidation above ~490 K ("H_2 2nd"). Once the sample was activated by the execution of CO oxidation, the H_2 oxidation activity was not changed significantly by repeated CO oxidation or H_2 oxidation. On the other hand, the conversion curve for CO oxidation after H_2 reduction was affected by neither CO oxidation nor H_2 oxidation.

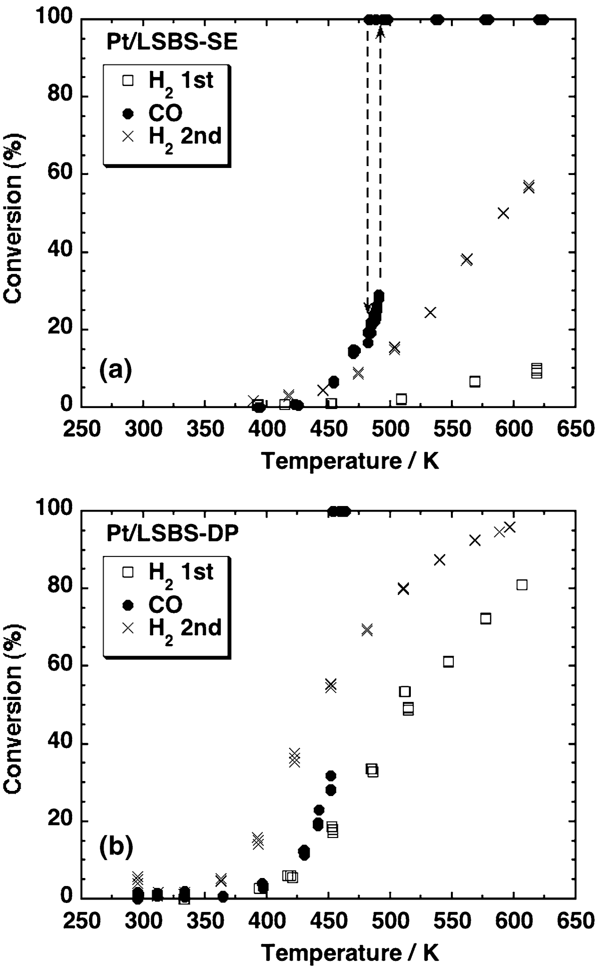

Fig. 2 CO and H_2 conversions versus reaction temperature over Pt/LSBS prepared by the (**a**) solid-phase elution or (**b**) deposition-precipitation methods. The oxidation reactions were conducted separately in the sequence "H_2 1st," "CO," and "H_2 2nd"

X-ray absorption fine structure (XAFS) analyses of Pt/LSBS have revealed that Pt is incorporated mainly in the B-sites (ScO_6 octahedral sites) of the perovskite structure [5]. The slight shift of the peak to lower energy in Fig. 3 after reduction indicates the partial reduction of the ionic Pt. The maximum amount of reduced Pt was estimated to be 25% of the total Pt. As shown in Fig. 4, ionic Pt was observed by X-ray photoelectron spectroscopy (XPS) before the H_2 reduction. After the reduction, peaks for metallic Pt appeared, whereas those for ionic Pt decreased in intensity [5, 6]. Pt metal particles as large as 2 nm were recognised by transmission electron microscope (TEM) after the H_2 reduction, whereas only the perovskite lattice was observed before the sample was reduced by H_2. These

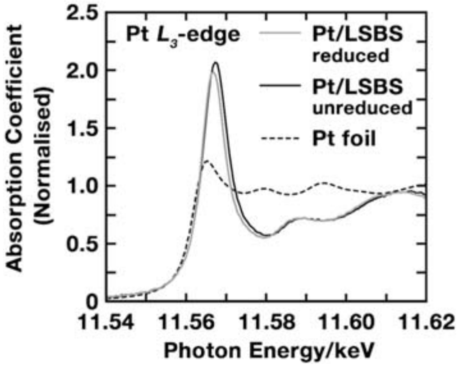

Fig. 3 X-ray absorption near edge structures of the Pt L_3-edge for Pt/LSBS, as well as for Pt foil (dotted line), before (black solid line) and after (grey line) reduction by H_2 at 550 K

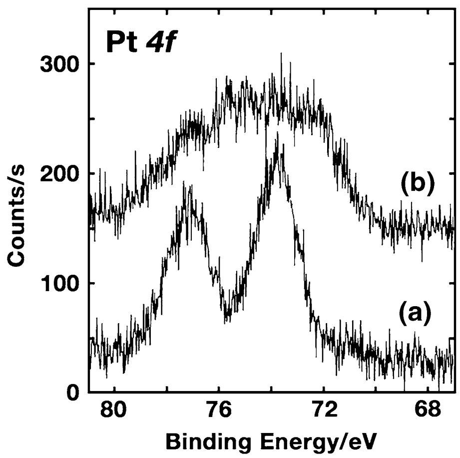

Fig. 4 X-ray photoelectron spectra for Pt/LSBS (**a**) before and (**b**) after reduction by H_2 at 550 K

results indicate that the Pt eluted into the perovskite lattice in the ionic state partly emerged as a result of the H_2 reduction to form the Pt nanoparticles supported on the perovskite surface. It should be stressed that the Pt nanoparticles were obtained by the SE method from the metallic Pt foil via the ionic state, despite the low ionisation tendency of Pt.

To investigate the effect of the preparation method, Pt/LSBS was prepared also by a conventional liquid-phase technique. Figure 2b shows the conversion curves for CO and H_2 oxidation over Pt/LSBS prepared by the DP method [7]. The activity of Pt/LSBS-DP for CO oxidation was slightly higher than that of Pt/LSBS-SE, whereas the former showed much higher activity for H_2 oxidation than the latter. A little increase in H_2 conversion after CO oxidation ("H_2 2nd" in Fig. 2b) was observed for Pt/LSBS-DP. Catalytic activities of Pt/LSBS-SE and Pt/LSBS-DP for CO and H_2 oxidation are compared in Fig. 5 with those of Pt deposited on perovskite without Ba, that is, $(La_{0.8}Sr_{0.2})ScO_{3-\delta}$, denoted by LSS, as well as conventional Pt/TiO_2 and Pt/Al_2O_3 catalysts prepared by the DP method. Only Pt/LSBS-SE showed superior CO oxidation activity.

Because no substantial catalytic activity was observed for unreduced Pt/LSBS-SE, we consider Pt cations in the perovskite lattice to be inactive for CO or H_2 oxidation by themselves, though the catalytic oxidation of CO was observed for the ionic Pt in $Ba_{12}[Ba_xPt_{3-x}]Pt_6O_{27}$ [8]. Judging from the large difference in conversion between Pt/LSBS-SE and Pt/LSBS-DP (compare Fig. 2a and b), the unique activity of Pt/LSBS-SE cannot be explained by a simple support effect of LSBS, although the proton conductivity of LSBS, as well as that of LSS, might suggest strong interaction of the support oxides with H_2 [5, 9]. Note that the larger part of Pt still exists as cations in the perovskite lattice even after the reduction of Pt/LSBS-SE [Fig. 3], in spite of the drastic change in colour, whereas all of the Pt is considered to form nanoparticles on the oxide surface in Pt/LSBS-DP. These results suggest that the Pt cations in perovskite may affect the catalytic activity of the Pt nanoparticles supported on LSBS, although their appearance on the surface was similar to that for the conventional supported Pt catalysts. Table 1 shows results of the CO pulse chemisorption for the representative catalyst samples. CO adsorption on Pt/LSBS-SE was considerably little, whereas Pt dispersion for Pt/LSBS-DP was comparable to that for Pt/Al_2O_3-DP. This indicates a quite low number of Pt nanoparticles on the surface and/or reduced ability of CO adsorption for Pt/LSBS-SE. Turnover frequencies per CO adsorption site for CO oxidation at 450 K were calculated to be 3.3 and 0.8 s^{-1} for Pt/LSBS-SE and Pt/LSBS-DP, respectively. These may indicate alternation of the active sites, for example, electronic influence of the Pt cations in the perovskite lattice on the surface Pt nanopartilces, while vacancy or distortion caused by an excess of the A-site cations might also affect the catalytic properties of Pt nanoparticles.

In the literature, it was reported that the partial substitution of B-sites by Pt promoted the CO oxidation over perovskite oxides [10, 11]. More recently, Tanaka et al. reported the reversible movement of Pd, Rh, and Pt into and out of the perovskite lattice for self-regenerating catalysts, where noble metals occupy the perovskite B-sites after reduction at 1273 K and come out of the lattice by oxidation at the same temperature [12, 13]. In the case of Pt/LSBS-SE, incorporation of Pt cations at 1898 K and formation of Pt nanoparticles above 550 K were observed.

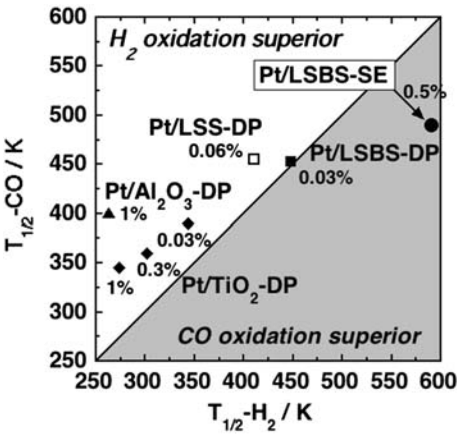

Fig. 5 Temperatures for 50% conversion of CO ($T_{1/2}$-CO) versus those for 50% conversion of H_2 ($T_{1/2}$-H_2) plotted for Pt/LSBS-SE, Pt/LSBS-DP, Pt/LSS-DP, Pt/TiO_2-DP, and Pt/Al_2O_3-DP, together with the loading amount of Pt (wt %). $T_{1/2}$-H_2 values after CO oxidation ("H_2 2nd" in Fig. 2) were used in the plot. In the case of discontinuous conversion curves, $T_{1/2}$-CO was defined as the average of the temperature of the upward conversion jump (on heating) and that of the downward conversion jump (on cooling)

Table 1 Amounts of CO adsorption and Pt metal dispersions for the supported Pt catalyst samples determined by the CO-pulse method, assuming unity stoicheiometry factor

Catalyst	Pt loading (wt%)	CO adsorption (cm^3/g-cat)	Pt dispersion (%)	Average pt size (nm)
Pt/LSBS-SE	0.5	0.001	0.3	–[a]
Pt/LSBS-DP	0.03	0.019	56.1	2.0
Pt/Al_2O_3	1.0	0.515	44.8	2.5
Pt/TiO_2	1.0	1.104	96.1	1.2

Measurements were carried out at 300 K, after the oxidation and subsequent reduction at < 523 K. Average Pt sizes were estimated from the CO adsorption by assuming spherical Pt particles. [a] Estimation of average Pt size for Pt/LSBS-SE, where larger part of Pt still exists as cations in the perovskite lattice, resulted in more than a few hundred nm, while Pt particles of ~2 nm were observed by TEM

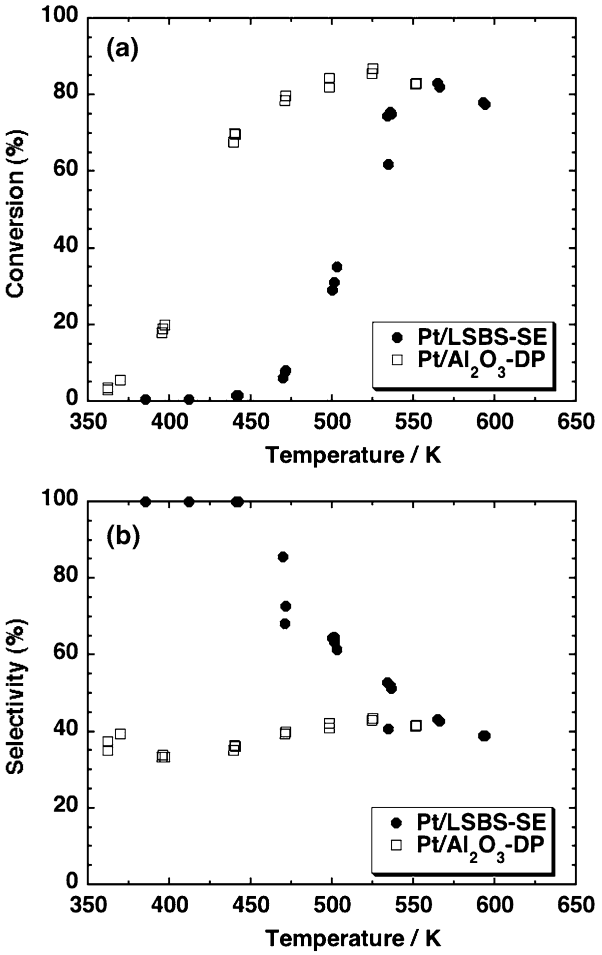

Fig. 6 (**a**) CO conversion and (**b**) selectivity to CO_2 for the PROX reaction over 0.5 wt % Pt/LSBS-SE and 1 wt % Pt/Al_2O_3-DP

Moreover, Pt has an affinity for Ba and did not actually elute into LSS. Pt was also eluted into other Ba-containing perovskeites, such as $(La_{0.7}Sr_{0.2}Ba_{0.1})CoO_{3-\delta}$ or $Ba(Zr_{0.8}Y_{0.2})O_{3-\delta}$, and exhibited higher activity for CO oxidation than that for H_2 oxidation. These findings suggest the mobility of Pt in the vicinity of the LSBS surface, which might affect its catalytic activity, although a drastic change in structure of Pt/LSBS-SE is not expected during oxidation reactions on the basis of observed stable catalytic activities.

Activities of Pt/LSBS-SE and Pt/Al_2O_3-DP for PROX reaction are shown in Fig. 6. Although CO oxidation was superior over Pt/LSBS-SE under separate oxidation conditions, a result opposite to that over Pt/Al_2O_3-DP, the PROX performance of Pt/LSBS-SE was similar at 550 K to that of Pt/Al_2O_3-DP. At lower temperatures, smaller CO conversion was observed for Pt/LSBS-SE, probably because of the smaller amount of Pt nanoparticles and the lower surface area of LSBS. H_2 oxidation over conventional Pt catalysts is known to be suppressed in the presence of CO [14]. In contrast, the activity of Pt/LSBS-SE for H_2 oxidation over Pt/LSBS-SE increased after separate CO oxidation [Fig. 2a], which might contribute to the enhancement of H_2 conversion in the presence of CO. This behaviour is also opposite to that of Pt/Al_2O_3-DP and confirms the uniqueness of the catalyst.

4 Conclusions

We found that Pt/LSBS perovskite prepared by the SE method shows higher catalytic activity for CO oxidation than for H_2 oxidation under separate reaction conditions, which is opposite to the behavior of conventional Pt catalysts. The unique activity appeared when ionic Pt in the perovskite lattice was partly reduced to Pt nanoparticles and may be attributed to the effect of Pt cations in the LSBS lattice on the Pt nanoparticles supported on LSBS. We are planning spectroscopic studies to investigate both the electronic states of Pt/LSBS and the adsorption states of CO.

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