Synergistic effect of palladium and oxygen vacancies in the Pd/perovskite catalysts synthesized by the spc method

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Abstract: A series of oxygen-deficient perovskite-supported palladium catalysts were prepared by the "solid phase crystallization"(spc) method and investigated with XRD, TPR, TPD, TEM, XPS, BET analysis and CO oxidation. It was found that Pd/perovskite catalysts synthesized by the spc method were more active for CO oxidation than the calcined $LaCo_{0.95}Pd_{0.05}O_3$, where Pd dispersed in the solid solution. H_2-reducing treatment in the spc method could yield not only high-dispersed fine Pd particles on the perovskite surface but also oxygen-deficient structure. In these perovskite-supported Pd catalysts, oxygen vacancies adsorbed, activated and supplied oxygen to the active Pd sites, where the oxidation occurred with adsorbed CO. The high activities were due to the cooperative action of Pd and oxygen vacancies.

Keywords: Pd; perovskite; oxygen vacancies; adsorbed oxygen; spc method; CO oxidation

Introduction

Perovskite-type oxides(ABO_3) are excellent catalysts for various reactions and easy to synthesize at lower cost and with great thermal stability up to high temperatures (Voorhoeve, 1977; Viswanathan, 1992). A key feature of ABO_3 is the availability of multicomponent matrixes, which can be obtained by partial substitution of cations A and/or B(Zhou, 2003). Especially, incorporating noble metals into the perovskite structure results in the stabilization of the metal against sintering, volatilization, or solid-state reaction with the substrate. Some enhancement in activity of the simple perovskite can also be achieved when small amounts of noble metals are incorporated (Peña, 2001; Nishihata, 2002; Zhou, 2002). In such a solid solution, however, most of the noble metals are in the bulk rather than the surface and the activities are limited.

Supported metal particles are commonly used heterogeneous catalysts. The active catalytic material is dispersed as small particles in order to maximize surface area (Giorgi, 2002). However, most of these catalysts have been conventionally prepared by wet impregnation of different supports and dispersed metal particles frequently tend to sinter at high temperature resulting in a deactivation. Most recently, Takehira (Takehira, 2002) applied a so-called "solid phase crystallization"(spc) method for the preparation of supported metal catalyst. Use of the precursors containing homogeneously distributed metal in the crystal structure, which on further calcination and reduction, may result in the formation of highly dispersed and stable metal particles on the surface. One kind of the precursors he used was perovskite-type oxides. Reducing treatment can modify the oxidation state of the metal located at the B site, which in many cases can be reduced to the metallic state, and a well-characterized "metal on oxide" solid can be obtained (Petunchi, 1990;

Crespin, 1981). It is the same case for the noble metal-containing perovskites. Guilhaume *et al*.(Guilhaume, 1996) reported that restructuration of $La_2Cu_{1-x}Pd_xO_4$ catalysts occurred under reacting conditions, leading to a more active state; this activation corresponded to destruction of the initial mixed-oxide structure, with formation of highly dispersed metallic palladium and Cu_2O particles. Tanaka *et al*. (Tanaka, 1995; 2001; Nishihata, 2002) found that the formation of Pd solid solution into perovskite crystals also depended on atmospheres. It appeared that a high state of dispersion was maintained as Pd repeatedly forms solid solutions in the perovskite crystal or segregates out from the crystal depending on the fluctuation of redox conditions and temperatures in automotive catalyst ambience. In fact, most of the ABO_3 does not reduce directly to simple oxides and metal, but rather proceeds to final products through the formation of intermediate oxygen-deficient structures (Sis, 1973). So after treatment under a controlled reducing atmosphere it is possible to generate oxygen-deficient provskite-supported palladium catalysts. Despite this, understanding of the activity-structure relationship of these catalysts is still quite limited.

In this work, perovskite-type oxide($LaCo_{0.95}Pd_{0.05}O_3$) was chosen as the precursor and a series of Pd/perovskite catalysts were synthesized by the spc method. CO oxidation as a model reaction was investigated to provide some insights into the activity-structure relationship of these catalysts.

1 Experimental

1.1 Catalyst preparation and characterization

$LaCoO_3$ and $LaCo_{0.95}Pd_{0.05}O_3$ perovskite-type materials were prepared from citrate precursors. A concentrated solution of metal nitrates and/or $PdCl_2$ was mixed with an aqueous solution of citric acid, by fixing at unity the molar ratio of citric acid to the total metal cations. Water was

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evaporated from the mixed solution at 90 ℃ until a viscous gel was obtained. The gel was heated overnight at 120 ℃, and then slowly calcined at 850 ℃ for 5 h. Both the calcined $LaCoO_3$ and $LaCo_{0.95}Pd_{0.05}O_3$ were black. Pd/perovskite catalysts were synthesized by the spc method as follows. A nitrogen-carried 5 vol% H_2 gaseous mixture was used as a reducing gas. The calcined $LaCo_{0.95}Pd_{0.05}O_3$ particles were placed in quartz fixed bed reactor, flushed by the reducing gas, reduced at certain temperature for 2 h and then cooled down to room temperature. Four catalysts were named P2, P3, P4 and P5 corresponding to the reducing temperatures, 250, 300, 400 and 500 ℃, respectively. It should be stated that after H_2 treatment all the samples turned olive green. However, they turned black quickly when they were taken out from the treatment reactor at room temperatures.

BET-surface areas of catalysts were measured by N_2 adsorption using the single point method and the results are shown in Table 1. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-RB diffractometer with Cu $K\alpha$ radiation. TEM measurements with EDX analysis were performed by a H8100 transmission electron microscope system. XPS measurements were conducted on a VG ESCA LAB 220 i-XL system with Al $K\alpha$ radiation under UHV(5×10^{-9} Pa), calibrated internally by carbon deposit C(1s) binding energy (BE) at 284.6 eV. Surface Palladium concentrations on the catalysts were measured through the pulse adsorption of H_2 in a flow of helium. At first, the catalyst was reduced at 150 ℃ in a nitrogen-carried 5 vol% H_2 gaseous mixture for 1 h, switched to pure He and the system was thoroughly flushed for 0.5 h, then cooled down to room temperature. H_2 pulses were injected until the quantity of the exit H_2 pulse reached a steady value. The surface Pd concentrations were calculated from the total H_2 uptake based on the assumption that one H atom adsorbed per metal surface atom.

1.2 H_2-TPR and O_2-TPD

Hydrogen temperature-programmed reduction (H_2-TPR) of catalyst was conducted on a fixed-bed continuous flow reactor connected with GC combination system. The catalyst sample(50 mg) was flushed with a nitrogen-carried 5 vol% H_2 gaseous mixture as a reducing gas for 0.5 h and then TPR test started. The temperature increased at a rate of 10 ℃/min. Change of hydrogen-signal was monitored using an on-line GC with a thermal conductivity detector(TCD). O_2-TPD runs were carried out in the same apparatus. After oxygen adsorption at 300 ℃ for 1 h, sample(150 mg) were cooled down to room temperature and the gas flow(50 ml/min) was then switched to pure He and the system was thoroughly flushed for 1 h. Finally, desorption was performed at a heating rate of 10 ℃/min. The oxygen evolution was monitored by TCD. Calibration was made by injecting 5 vol.% oxygen in helium.

1.3 Activity measurement

CO oxidation was carried out in a quartz fixed bed reactor. The reactor was placed in a tubular PID-regulated oven and the temperature was monitored with a Ni-Cr thermocouple positioned in correspondence to the catalyst bed. The catalyst powder(ca. 0.36 g) was crushed, sieved to 60—100 mesh. The gaseous flow rates were measured by mass flow meters and mixed at atmospheric pressure to obtain inlet concentrations of 1 vol.% CO, 2.5 vol.% O_2, N_2 as balance, with a space velocity of 55000 h^{-1}. Reaction temperature was raised at 1 ℃/min from 100 to 400 ℃, and product stream was analyzed by on-line GC, CO_2 being the only reaction product detected.

2 Results

2.1 XRD

The X-ray diffraction pattern obtained from the calcined $LaCo_{0.95}Pd_{0.05}O_3$ is shown in Fig. 1 and includes only the crystal phase of perovskite, which shows sharp and well-defined structure reflections. The patterns of P2, P3 and P4 are similar to that of the calcined $LaCo_{0.95}Pd_{0.05}O_3$ only perovskite structures can be observed. This indicates that the perovskite structure does not collapse when the reducing temperatures do not exceed 400 ℃. However, it is necessary to note that the intensity of diffraction peaks for the reduced samples is smaller than that for the calcined perovskite and increases with the increase in the H_2-reducing temperature, suggesting the modification of the solid under pretreatment conditions. The peak intensity of P5 is rather smaller. Moreover, a small amount of the very fine oxides(broad weak peaks indicated by the arrows in Fig. 1) can be observed. This indicates that the perovskite must be partially destroyed after reduced at 500 ℃. No lines corresponding to palladium oxide or metal can be observed for all the samples.
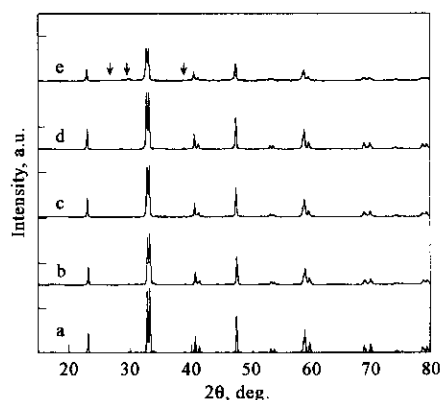

Fig.1   XRD patterns of catalysts: the calcined $LaCo_{0.95}Pd_{0.05}O_3$ (a), P2 (b), P3 (c), P4 (d) and P5 (e)

2.2 H_2-TPR

The TPR profile of the $LaCoO_3$ perovskite is given in Fig. 2 for comparison. There are two main reduction bands at

460 ℃ and 650 ℃. According to the experimental work of Lago et al. (Lago, 1997), the low temperature TPR peaks would be associated to a one-electron reduction process(Co^{III} + $e \rightarrow Co^{II}$) whereas the second step to a two-electron reduction process($Co^{II} + 2e \rightarrow Co^{0}$).
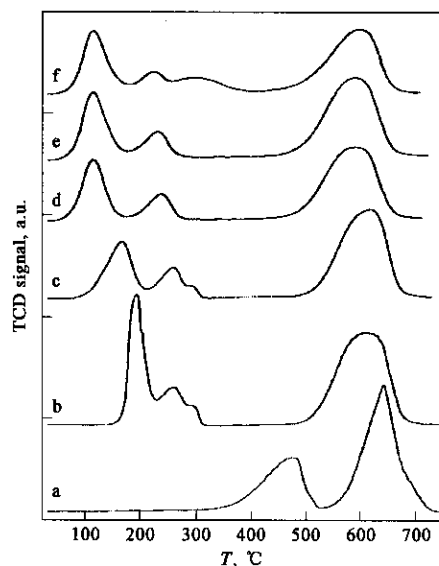

Fig.2 H_2-TPR profiles of catalysts: the calcined $LaCoO_3$ (a), the calicined $LaCo_{0.95}Pd_{0.05}O_3$ (b), P2 (c), P3 (d), P4 (e) and P5 (f)

The TPR profile of the calcined $LaCo_{0.95}Pd_{0.05}O_3$ shows three reduction peaks at 195, 250 and 600 ℃, respectively. The first peak can be assigned to $Pd^{II} \rightarrow Pd^{0}$ according to our previous study(Zhou, 2002), and the second to $Co^{III} + e \rightarrow Co^{II}$. The reduction temperature shifts to lower temperature and the high temperature peak become broader, suggesting the increasing reducibility of the Pd-containing perovskite. It can be concluded that palladium introduced by citrate process occupy B-sites of the perovskite and affect the properties of crystal oxygen in ABO_3 structure.

The TPR profiles of the catalysts prepared by the spc method(Fig.2 c-f) are similar to that of the calcined $LaCo_{0.95}Pd_{0.05}O_3$. The reduction peaks shifts to lower temperatures with the increase in the H_2-reducing temperature, and then keeps unchanged when the reducing temperature is above 300 ℃. Additionally, a new peak centered at 340 ℃ can be observed for P5. This can be assigned to the reduction of the

highly dispersed cobalt oxides indicated in the XRD pattern.

The samples of P3, P4 and P5, which had been reduced at 300, 400 and 500 ℃ respectively during preparation, should not been reduced below 300 ℃ during the TPR runs. However, this was not the case—the samples prepared by the spc method still could be reduced at temperatures below 300 ℃ during TPR. This is because that the samples prepared by the spc method can be reoxidized in air at room temperature. As stated in the experimental section, when the samples were taken out from the reducing treatment reactor at RT in air, the reoxidation was fast; the olive green color (Co^{II}) changed to black (Co^{III}) instantaneously (Crespin, 1981). And the reoxidation includes two processes, Co^{II}-$e \rightarrow Co^{III}$ and $Pd^{0} \rightarrow Pd^{II}$. Combined with the XRD results, the former process allows the restoration of the perovskite structure. However, the shift to low temperatures of the first peaks from TPR profiles indicated that the palladium cannot reenter the B-sites of perovskite after reoxidation at room temperature. Moreover, oxygen vacancies should be generated for electric charge compensation. So the oxygen-deficient provskite-supported palladium catalysts can be obtained by the spc method. And the size of the Pd species (metallic palladium or oxides) is mostly less than 3 nm because they cannot be detected by X-ray diffraction.

2.3   Surface Pd concentrations based on H_2 chemisorption

Table 1 lists the surface Pd concentrations of all the catalysts. Surface Pd concentrations were calculated by assuming a Pd/H = 1 stoichiometry. It can be seen from the data of Table 1 that an increase of the reduction temperature produces a decrease in the surface Pd concentrations (Guerrero-Ruiz, 2000): the calcined $LaCo_{0.95}Pd_{0.05}O_3$ < P5 < P4 < P3 < P2.

2.4   TEM

TEM observations of the catalysts are shown in Fig.3. The perovskite particles distributed between 100 and 300 nm for all the samples, and the H_2-reducing treatment has little effects on the particle size. The surface of the calcined $LaCo_{0.95}Pd_{0.05}O_3$ and P2 is smooth, while lots of protuberances are observed on P3 and P4. In the case of P5, there are new fine particles of about 10 nm adhered on the

Table 1   Characteristics of the catalysts and CO oxidation rates

Catalyst code	H_2-reducing temperature, ℃	Phase[a]	BET area, m^2/g	Surface Pd concentration[c], μmol/g	Amount of α-oxygen[d], μmol/g	T90 for CO oxidation, ℃	CO oxidation rate[e], μmol/(g·s)	TOF[f], s^{-1}
Calcined	—	P	4.3	5.4	71	300	0.17	0.031
P2	200	P	4.3	11.6	101	205	1.01	0.087
P3	300	P	4.4	10.0	139	188	3.85	0.386
P4	400	P	4.5	9.8	110	238	0.36	0.037
P5	500	P + S[b]	4.5	6.5	269	225	0.27	0.041

Notes: [a] Detected by XRD measurement, P = perovskite, S = simple oxides; [b] trace; [c] calculated from H_2 uptake at room temperature after H_2 treatment at 150 ℃; [d] the amount of α-oxygen determined at < 500 ℃ from O_2-TPD profile; [e] the rate calculated at 185 ℃; [f] the turnover frequency determined at 185 ℃ based on the surface Pd concentration

surface of larger perovskite particles. From EDX analysis(not shown here), it is found that the protuberances contain a large amount palladium, whereas the amount of Pd is relatively smaller in the new fine particles. The TEM images shows the occurrence of surface modification after H_2-reducing treatment during the spc preparation.
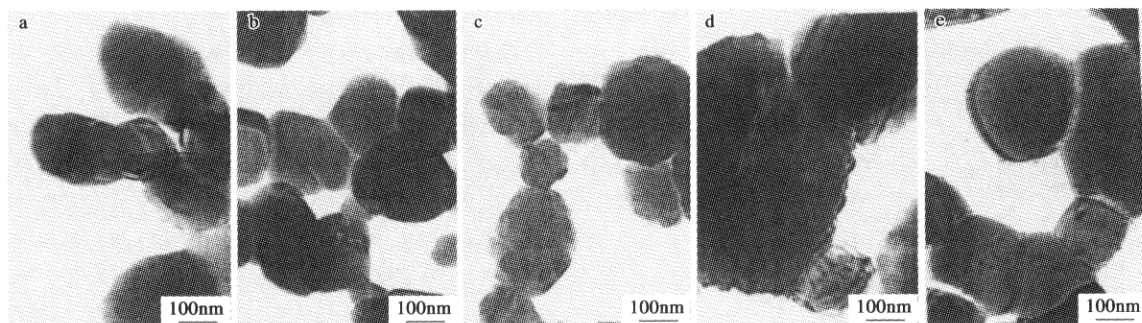

Fig.3   TEM images of catalysts: the calcined $LaCo_{0.95}Pd_{0.05}O_3$(a), P2 (b), P3 (c), P4 (d) and P5 (e)

2.5   Analysis of Pd by XPS

The state of Pd was analyzed by XPS and the results are shown in Fig.4. The values for metallic Pd, Pd^{II} and Pd^{IV} were 335.1, 336.8 and 337.8 eV, respectively(Tanaka, 2001; Zhou, 2002; Priolkar, 2002; Noronha, 2000).

In the calcined $LaCo_{0.95}Pd_{0.05}O_3$ catalyst(Fig. 4a), the peak of Pd 3 d appears at 336.8 eV with a shoulder at 337.8 eV. In fact, the perovskite-type $LaPdO_3$ has been synthesized already and an unnormal Pd^{III} state was obtained (Kim, 2001). Owing to its configurational instability, Pd^{III} has a strong tendency to decompose disproportionally into Pd^{II} and Pd^{IV}. The mixture of bivalence and tetravalence indicated that Pd is dispersed in the crystal of the calcined $LaCo_{0.95}Pd_{0.05}O_3$ perovskite(Tanaka, 2001). After reduced by H_2, Pd^0 can be observed(Fig.4b for P2 and Fig.4c for P3) and the intensity of metallic Pd increases with the increase in the reducing temperature. However, further increase in the reducing temperature leads to a decrease of metallic Pd and an increase of Pd^{II} without Pd^{IV} (Fig. 4d and Fig. 4e). Tanaka *et al*.(Tanaka, 2001) also found a transition of Pd state under redox atmosphere at high temperatures, ca. from 700 to 1000 ℃, and attributed this to Pd repeatedly integrated into solid solution and segregates out from the perovskite crystal. As stated before, reoxidation took place

only at RT in the present study and Pd could not reenter the solid solution at such a low temperature. Combining with results of XRD, TEM and TPR, it can be rationalized that reducing treatment at 500 ℃(ca. P5) can generate a cobalt-covered palladium structure where Pd can be easily reoxized even at room temperature.

2.6 O_2-TPD

Fig.5 shows the oxygen temperature-programmed desorption(O_2-TPD) profiles. The profiles can be generally divided into two groups, oxygen desorbed at low temperatures (< 500 ℃) and at high temperatures(> 500 ℃), although the transition from the former to the later is continuous and these two oxygen species are hardly distinguishable. The later, usually referred to as a β peak, is clearly lattice oxygen (Nakamura, 1981; Seiyama, 1992). The onset temperature of oxygen desorption and the peak shape of the former(α-oxygen), from the calcined $LaCo_{0.95}Pd_{0.05}O_3$, P2, P3, and P4, are about the same, indicating that the desorbed oxygen emanates from the same sites in all these samples(Ramesh, 1996). Lots of studies on A site substituted ABO_3 demonstrated that α-oxygen is accommodated in the oxygen vacancies and evolved in heating (Seiyama, 1992). The amounts of α-oxygen are presented in Table 1. The data in Table 1 show that the amount of α-oxygen increases with the H_2-reducing temperature, via a maximum(139 $\mu mol/g$) for P3 and then decrease. According to TPR results, P4 should contain more oxygen vacancies than P3. However, the α-oxygen amount of P4 is smaller than P3. This is mostly because that the defects become ordered after reduced at higher temperature; so a relatively stable structure is formed and less oxygen can be accommodated. In the case of P5, the shape of the α peak is quite different from that of the other catalysts and a relatively large quantity of desorbed oxygen can be obtained. It is clearly from another resource. Kirchnerova *et al*.(Kirchnerova, 2002) reported that Co_3O_4 could give more oxygen than Co-based perovskite during O_2-TPD runs. Combining with the XRD results, the α peak of P5 can be assigned mainly to decomposition of simple cobalt

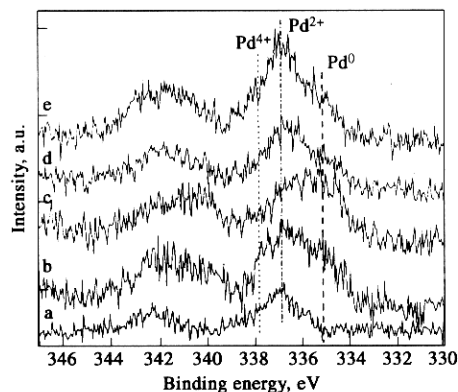

Fig.4   XPS Pd 3 d spectra of catalysts: the calcined $LaCo_{0.95}Pd_{0.05}O_3$(a), P2 (b), P3 (c), P4 (d) and P5 (e)
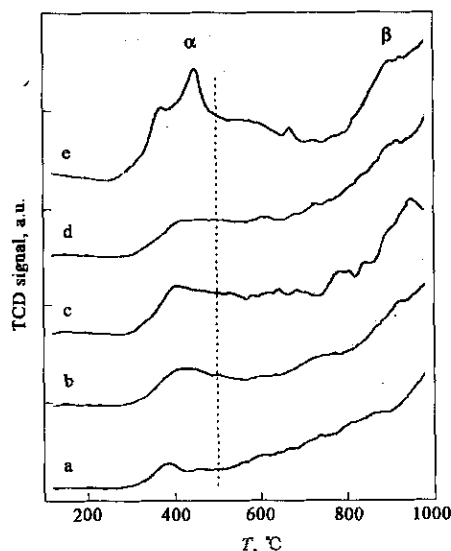
oxides.

Fig.5   Temperature-programmed desorption profiles of oxygen from catalysts: the calcined $LaCo_{0.95}Pd_{0.05}O_3$ (a), P2 (b), P3 (c), P4 (d) and P5 (e)

2.7   Catalytic activity of CO oxidation

Activities of Pd-containing perovskite catalyst for CO oxidation are shown in Fig. 6. Table 1 lists the T90, corresponding to 90% conversion of CO, for all the samples. The activitiy decrease in the order of P3 > P2 > P5 > P4 > calcined $LaCo_{0.95}Pd_{0.05}O_3$. In general, the catalysts prepared by the spc method are more active than the calcined perovskite. On the other hand, the reducing temperature applied in the spc method plays an important role in the catalytic activity. The activity first increases with the increase in the reducing temperature within 300℃, and then decreases when the reducing temperature is above 300℃; and a further increase in the reducing temperature, ca. 500℃, can lead to a slight increase in the activity. To compare intrinsic catalyst activities, we calculated from the CO conversion vs. temperature curves the reaction rates(μmol CO/(g catalyst · s)) and turnover frequencies (TOF per second) at 185℃; the values are shown in Table 1. CO oxidation rates increased drastically with increasing surface
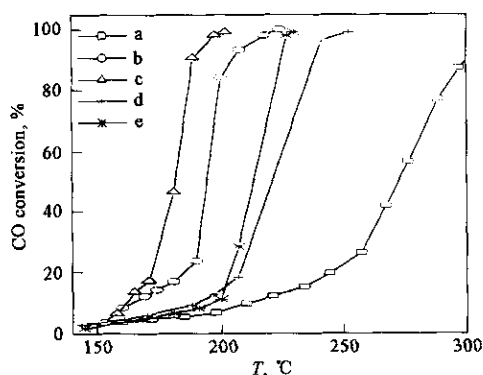

Fig. 6   Co light off curves for catalysts: the calcined $LaCo_{0.95}Pd_{0.05}O_3$(a), P2 (b), P3 (c), P4 (d) and P5 (e)

Pd concentrations. In contrast, the TOF values increased slightly with increasing surface Pd concentrations on all catalysts except P3 which was about 12 times higher than that measured on the calcined $LaCo_{0.95}Pd_{0.05}O_3$ catalyst.

3   Discussion

3.1   Surface Pd concentrations and catalytic activity

The CO oxidation reaction has generated considerable interest, not only due to its importance in terms of emissions control but also because its relative simplicity makes it an ideal, tractable heterogeneous catalysis problem. This reaction has been thought to be structure-insensitive for a long time (Ladas, 1981), but recent works on single-crystal surfaces and on supported clusters evidenced slight but real intrinsic size effects(Uetsuka, 1997; Watanabe, 1998).

In the present study, surface Pd concentrations of the catalysts prepared by spc method are higher than the calcined $LaCo_{0.95}Pd_{0.05}O_3$, and their activities are higher than that of the later. In addition, P2 and P3 are more active than P4 and P5, where surface Pd concentrations are relatively lower. However, the correlation between the activity and the surface Pd concentration is not so linear. For example, the surface Pd concentration of P2(5.78%) is higher than that of P3 (4.96 %), but the TOF of the former is lower than that of the later. This demonstrated the existence of other factor(s) that also affects the catalytic performance.

3.2   Adsorbed oxygen and catalytic activity

The reaction mechanism of CO oxidation reaction over noble metals has been described by a Langmuir-Hinshelwood model where molecularly adsorbed CO reacts with atomic oxygen on the surface, desorbing CO_2. Because CO adsorbs more strongly on the surface than molecular O_2, the surface of the catalyst is predominantly populated with adsorbed CO under reaction conditions, which inhibits the dissociative adsorption of oxygen (Rainer, 1997). So accelerating the dissociative adsorption of oxygen should be favorable for CO oxidation. It was reported that noble metals supported on oxide supports showed higher activity for CO oxidation at low temperatures, which was considered due to the strong affinity of the support to oxygen and the oxygen-providing ability to metal(Park, 2000; Imamura, 1995).

It is well known that oxygen-deficient perovskites desorb or adsorb a large amout of oxygen. The nature and reactivity of adsorbed oxygen may be greatly different from other oxygen which forms a rigid crystal lattice, because the adsorbed oxygen is more weakly bonded to metal cations than the normal lattice oxygen(Voorhoeve,1997; Seiyama, 1992). In this work, the result of O_2-TPD showed that two kinds of oxygen can be desorbed from perovskite at low temperature (< 500℃). One is accommodated in the oxygen vacancies, ca. the calcined $LaCo_{0.95}Pd_{0.05}O_3$, P2, P3 and P4; the other is from the decomposition of simple cobalt oxides, ca. P5.

Although the amount of α-oxygen is higher than all the others, P5 is only slightly active than P4 and much inferior to P2 and P3, indicating that oxygen accommodated in the oxygen vacancies are more active. Among the calcined $LaCo_{0.95}Pd_{0.05}O_3$, P2 and P3, the more the amounts of α-oxygen, the higher the activity. However, P2 is more active than P4, despite that the former desorbed less amounts of α-oxygen than the later.

Based on these considerations, the activity of the Pd-containing perovskite is determined not only by surface Pd concentrations but also oxygen vacancies which can accommodate large amounts of active oxygen. Excellent activity can be obtained on the catalyst which has both higher surface Pd concentrations and higher oxygen vacancies, ca. P3. In this catalyst, the oxygen-deficient perovskite has good ability to adsorb, activate and supply oxygen to the active Pd sites where the oxidation occurs with adsorbed CO.

4 Conclusions

Pd/perovskite catalysts prepared by spc method showed the higher catalytic activity oxidation of CO than the calcined perovskite with Pd dispersed in the solid solution.

Synergistic effect of palladium and oxygen vacancies has been found in the Pd/perovskite catalysts. Oxygen vacancies can adsorb, activate and supply oxygen to the active Pd sites where the oxidation occurs with adsorbed CO. Good activity can be obtained on the catalyst, which has both higher surface Pd concentrations and higher oxygen vacancies.

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