Fe,Pd Co-Incorporated LaCoO3 Perovskites: Modification of Thermal Stability and Catalytic Activity for Gasoline Vehicle Exhaust Purification (Postprint)

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Abstract

A series of LaCo0.95-xFexPd0.05O3 (x = 0, 0.1, 0.2, 0.3) perovskite-type catalysts have been prepared by a modified sol-gel method. Their structures and physicochemical properties have been studied by powder X-ray diffraction (PXRD), transmission electron

Full Text

Preamble

A series of LaCo . - Fe Pd . O (x = 0, 0.1, 0.2, 0.3) perovskite-type catalysts have been prepared by a modified sol-gel method. Their structures and physicochemical properties have been studied by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), the Brunauer-Emmett-Teller (BET) isotherm technique, and temperature-programmed reduction (TPR). Structural characterization showed that Fe had been successfully doped into the perovskite lattice and that Fe doping improves the stability of LaCo . Pd . O . A study of the catalysts showed that aged samples maintain the perovskite structure. They all exhibited similar catalytic performance, which has been ascribed to the similar state of palladium at the surface of the catalysts. Of these as-prepared catalysts, the Fe-doped perovskites achieved better catalytic activities than LaCo . Pd . O , and LaCo . Fe . Pd . O showed the optimal catalytic performance for vehicle emission purification.

Keywords: Heterogeneous catalysis / Environmental chemistry / Perovskites / Iron / Doping / Palladium

Introduction

As the growing use of automobiles aggravates environmental pollution caused by automobile exhausts, increasingly stringent tail gas exhaust standards have been put forward by many countries. This trend has led to intense research into catalysts designed to abate toxic emissions, mainly carbon monoxide, unburned hydrocarbons, and nitrogen monoxide from gasoline vehicles. The traditional and most commercialized three-way catalysts are based on noble metals, for example, platinum, palladium, and rhodium [1,2]. Three-way catalysts (TWCs) are considered to be the most efficient for eliminating poisonous emissions. However, the use of catalysts based on noble metals is limited by restricted resources, high price, and particle growth at high temperatures. Perovskite-type catalysts, which have considerable thermal stability and low cost, were found to have potential for automobile emission purification and have attracted considerable attention since the 1970s [3].

The catalytic properties of perovskites with the general formula of ABO , in which the A sites are usually filled with rare-earth metal cations and the B sites are usually occupied by transition-metal cations, can be adjusted by selecting different metal ions at the A and B sites [4,5]. The perovskite-type catalysts that have been studied for TWC applications mainly have La at the A sites. Most of the research in this area has been focused on adjusting the cations at the B sites because the catalytic properties of these types of catalysts greatly depend on the nature of B-site ions [6,7]. For example, perovskite-type oxides with transition-metal cations such as Cu, Mg, Cr, Fe, Co, and Ce at the B sites have been investigated [8–14]. Of these catalysts, LaCoO as a typical perovskite has attracted widespread attention and has been reported as an excellent catalyst for many reactions, for example, CH oxidation, CO oxidation, and NO reduction [15–20]. Recently, a mesoporous perovskite synthesized by the hard template method was studied and highlighted for its high NO reduction efficiency and high NO to N selectivity [20]. In addition, LaCo . Pd . O , which has a palladium content of less than 30% that of commercial catalysts, has also been intensively investigated due to its superior catalytic performance compared with LaCoO [9,21,22].

However, the low structural stability of Co-based perovskites under a reducing atmosphere at high temperatures limits their application because decomposition of the catalysts is likely to influence the catalytic process resulting in unstable catalytic performance [23,24]. The partial substitution of Co by other ions such as Fe and Mn is considered to be a means to improving its stability as well as catalytic properties [22,25–27]. Rodríguez et al. studied the TWC applications of LaFe . Co . O with Pd impregnated onto or integrated into the catalyst (LaFe . Co . Pd . O and Pd-LaFe . Co . O , respectively) and found that LaFe . Co . Pd . O exhibited better NO reduction activity than Pd-LaFe . Co . O [27]. However, such reports paid more attention to the state of Pd in the perovskite and their activity. The effect of doping elements into the B site on the structure and thermal stability of the perovskite has not been systematically studied.

In this work, a series of LaCo . – Fe Pd . O (x = 0, 0.1, 0.2, 0.3) perovskites were synthesized and their catalytic performance and physicochemical properties systematically studied to reveal the influence of Fe doping on the properties of the perovskites. Furthermore, Fe-doped catalysts aged at high temperatures in air were studied to explore their potential application for automobile exhaust purification.

Results and Discussion

Structural Characterization of Fresh and Aged Catalysts

To study the effect of Fe doping on the structures of the as-prepared perovskites, powder X-ray diffraction patterns were recorded under two different conditions: fresh LaCo . – Fe Pd . O (Figure 1 [Figure 1: see original paper], a) and LaCo . – Fe Pd . O after one catalytic cycle (Figure 1, b). All the diffraction peaks of the fresh catalysts can be assigned to a single-phase LaCoO perovskite structure (JCPDS 25-1060), which demonstrates that the perovskite structures are well maintained after the partial substitution of Co by Fe and Pd. No peaks corresponding to impurities were observed. In addition, an enlarged scale of the strongest diffraction peaks of the fresh catalysts (2 range: 30–38°) is shown in Figure 1 (a) and reveals a slight shift to a lower 2 as the value of x increases, which has been ascribed to the larger ionic radius of Fe compared with that of Co and indicates that Fe has been successfully doped into the perovskite lattice. Furthermore, SEM/EDS mapping results showed that Pd is well distributed in the perovskites (see Figure S1 in the Supporting Information). The powder XRD patterns of the catalysts recorded after exposure to simulated automobile emissions show that the Fe-doped samples are still single perovskite crystals whereas the Fe-free sample has decomposed to several metal oxides instead of maintaining the perovskite structure, which demonstrates that Fe doping enhances the structural stability of the perovskite catalysts under reaction conditions.

The reduction behavior of the as-prepared catalysts is shown in Figure 2 [Figure 2: see original paper] along with the behavior of LaCoO as a reference. Two main peaks at 623 and 813 K are observed for LaCoO , which have been assigned to the reduction of Co^{3} to Co^{2} and Co^{2} to Co respectively [9,28,29]. After the partial substitution of Co by Pd, the two peaks appear at significantly lower temperatures, especially the peak in the low-temperature region, which is due to the Pd substitution improving the reduction performance of the catalyst. The minor peak observed at 345 K is considered to result from the reduction of the palladium incorporated into the perovskite [30–32]. Further partial substitution of Co by Fe also leads to a decrease in the temperature of the reduction peak in the low-temperature region, although the effect is not as significant as the Pd doping. However, the impact of Fe doping on the peak in the high-temperature region is more obvious: the peak gradually moves towards higher temperatures as the value of x increases and its shape becomes less symmetric owing to the reduction of Fe^{3} to Fe^{2} in the bulk [22]. For samples with $x > 0$, the former observation indicates that Fe doping may restrain the reduction of Co^{2} to Co and the latter is further proof for the successful incorporation of Fe into the perovskite structure. Interestingly, the sample with $x = 0.3$ shows the lowest reduction temperature of Pd . This indicates that the catalyst with $x = 0.3$ may give the best catalytic performance, which the subsequent light-off experiment verifies, as shown below.

Effect of High-Temperature Aging

The properties of catalysts for TWC applications can be strongly affected by the emission atmosphere at high temperatures [33]. To further investigate the catalytic performance of Fe-doped catalysts, aging experiments were conducted by thermally treating the samples at 1223 K for 6 h in air, which is an oxidation atmosphere and contains a similar oxygen concentration (about 20%) to exhaust gases discharged when the deceleration fuel cut-off technology is activated during deceleration of the engine [34]. The aged catalysts were then characterized and their catalytic activity assessed.

The catalysts were characterized to investigate the effect of aging. As seen in Figure 3 [Figure 3: see original paper], the powder XRD patterns of the aged catalysts are consistent with the peaks exhibited by LaCoO perovskite crystals (JCPDS 25-1060). Hence, the aging process does not have any detectable effect on the bulk phase of the as-prepared catalysts, and the peaks in the enlarged view show that the perovskites become purer after the thermal treatment at high temperature. In addition, the morphologies of the samples pre- and post-aging were studied by transmission electron microscopy (TEM; Figure 4 [Figure 4: see original paper]). It can be seen that there is severe agglomeration after aging as the particle size grows from about 100 nm to nearly 200 nm. The surface area data presented in Table 1 further supports the phenomenon of agglomeration by the reduced surface area of the catalyst after aging. The catalyst with $x = 0.3$ suffered the smallest loss of surface area of the four samples, decreasing from 4.56 to 1.95 m^{2} g^{1}. Because the specific surface area of a catalyst can have an impact on the catalytic activity by influencing the number of active sites [35], the decreased surface areas caused by aging may have an influence on the catalytic performance of the aged catalysts.

H temperature-programmed reduction (TPR) experiments were also conducted on the aged catalysts. Comparing the results obtained for the fresh (Figure 2) and aged catalysts (Figure 5 [Figure 5: see original paper]), the reduction peaks for the fresh catalysts in the range 333–523 K are shifted to higher temperatures after aging, but there is no obvious change in the peaks in the range 773–1073 K. This indicates that the aging process impedes the reduction of Co^{3} to Co^{2} and Pd^{2} to Pd (as shown in the analysis of XPS spectra below), especially for the sample containing no iron. However, the reduction temperatures of palladium in the Fe-doped samples are all lower than that of palladium in LaCo . Pd . O , which again indicates the enhancement of catalytic activity caused by Fe doping.

Surface Analysis by XPS

The surface states of the fresh and aged catalysts were studied by X-ray photoelectron spectroscopy (XPS) and the surface elemental components of the perovskites are shown in Table S1 in the Supporting Information. The Pd 3d XPS spectra displayed in Figure 6 [Figure 6: see original paper] show two doublets for each fresh catalyst, and the low and high binding energy peaks of each doublet are characteristic of Pd 3d / and Pd 3d / respectively, which indicates the presence of two different Pd species. The decomposition of the Pd 3d spectra shows two components of Pd 3d / peaking at 336.6/339.3, 337.0/338.4, 336.7/338.6, and 336.9/338.9 eV, corresponding to x = 0, 0.1, 0.2, and 0.3, respectively. The Pd 3d / components at 335–336, 336–337, and above 338 eV have been separately assigned to metallic palladium, Pd^2 , and Pd , respectively [36]. Thus, it can be concluded that there are two states of palladium in the fresh catalysts, that is, Pd^2 and Pd , which means Pd has been successfully doped into the B site of the perovskite lattice during the synthesis.

In addition, after simulating and calculating the different compositions of the peaks, it was found that the percentage of Pd increases with Fe content (Table 2), especially when the value of x increases from 0 to 0.2. This explains the decrease in the reducing temperature in the low-temperature region caused by Fe substitution in the TPR results (Figure 2). Nevertheless, only one pair of peaks is observed in the Pd 3d XPS spectra of the aged catalysts. The Pd 3d / peaks appear at about 337.5 eV, which has been ascribed to PdO species, as previously reported [36]. These data reveal that the Pd in the perovskite is unstable during the thermal treatment in air, with the highly dispersed Pd in the fresh catalysts agglomerating at the surface after aging. Although no other oxides are detected in the XRD patterns of the aged samples due to a much lower Pd content compared with other B-site atoms, it can still be confirmed that there is a distortion of the perovskite structure at the surface of the aged catalysts because the bulk phase has become more pure, as proved by XRD. This is in agreement with the report of Pan and co-workers who deemed that precious metal ions in perovskite material can only move a few nanometers [37].

Catalytic Performance Evaluation

The catalytic performances of the pre- and post-aged LaCo . - Fe Pd . O (x = 0, 0.1, 0.2, 0.3) samples were evaluated in a simulated automotive emission gas mixture under a theoretical air/fuel (A/F) ratio of 14.7. Figure 7 [Figure 7: see original paper] shows the conversions of the three main pollutant emissions, CO (Figure 7, a, b), C H (HC, Figure 7, c, d), and NO (Figure 7, e, f). For the fresh catalysts (Figure 7, a, c, e), the T and T values of the sample with x = 0 for HC removal are 721 and 743 K, respectively, which are both higher than the T and T values of the Fe-doped samples. As the Fe content increases, both T and T for HC decline. The conversion of NO shows a similar trend, except that the conversion of HC corresponding to LaCo . Pd . O fell to about 83% after reaching its highest level at just over 95%. This decline may be caused by the structural instability of LaCo . Pd . O revealed by the PXRD experiments (Figure 1, b). These results suggest that Fe doping can improve the catalytic performance of the removal of HC and NO to some extent.

Interestingly, the NO conversion for all samples fluctuates from about 473 to around 673 K, and then experiences a sharp increase from approximately 15 to 100%. Moreover, the inflection points of these curves occur at exactly the same points at which the slope of the HC conversion changes, which implies a possible relationship between the oxidation of HC and the reduction of NO. Looking at the whole catalytic performance of the catalysts for the removal of HC and NO, it is easy to see that the samples with x = 0.2 and 0.3 behave quite similarly, and, as discussed before, the Pd contents in these two samples are quite similar and the Pd contents in all the Fe-doped catalysts are higher than that in the sample with x = 0. Thus, we speculate that Pd may play an important role in the catalysis of HC and NO removal. In addition, for the oxidation of CO, the Fe-doped catalysts all exhibit much better catalytic activity as their T values are all below 573 K; thus, as shown in Figure 7 (a), Fe doping significantly improves the catalytic activity. However, the improvement does not correlate with the degree of Fe doping because the ignition temperature of the four catalysts decreases in the order $x = 0.2 > x = 0.1 > x = 0.3 > x = 0$.

After aging, the light-off performances of the catalysts (Figure 7, b, d, f) are quite different from those of the fresh catalysts. Although both the T and T values of the fresh catalysts for NO conversion are higher than those of the aged catalysts, the complete conversion of NO is achieved above 873 K for all the aged catalysts, which is much higher than the corresponding temperature (below 773 K) for the fresh catalysts. Comparing the catalytic performances of the pre- and post-aged catalysts, fluctuation in the low-temperature region of the NO light-off curves of the aged catalysts is less obvious but the inflection points still correspond to those on the HC light-off curves, which is further proof of the relationship between the oxidation of HC and NO reduction mentioned above. After aging at high temperature, the CO light-off curves of all the catalysts retain similar shapes to those of the fresh catalysts, but the ignition temperature is boosted by 40–100 K. Also, the catalysts with different Fe contents show similar catalytic performances after aging at high temperature. Combining the results of the XPS analysis and the catalytic experiments, it may be concluded that perovskite itself without a noble metal shows good activity towards CO oxidation, but that palladium on the surface plays a crucial role in eliminating NO and HC. The former is in accord with previous reports [38,39]. In addition, the similar catalytic activities of the aged samples in contrast to those of the fresh catalysts may be a result of the presence of Pd in the same state at the surface of the aged catalysts. However, the sample with x = 0.3 has the lowest ignition temperatures for the three pollutants compared with the other three catalysts.

Experimental Section

Synthesis of the Catalysts

A series of LaCo . – Fe Pd . O (x = 0, 0.1, 0.2, 0.3) were prepared by using a modified sol-gel methodology, as reported in our previous work [40]. Stoichiometric amounts of La(NO) ·6H O, Co(NO) ·6H O, Fe(NO) ·9H O, and Pd(NO) were dissolved in deionized water with vigorous stirring. After the solution became homogeneous, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were added to give an EDTA/CA/total-metal-ion molar ratio of 1:2:1. The resulting mixture was dehydrated in a water bath at 358 K whilst stirring until it formed a viscous liquid gel, which was subsequently dried in an oven for over 12 h. Calcination of the dried precursor was performed in two steps: the first step was performed at 823 K for 2 h in air to eliminate organic components and the second at 973 K for 5 h to form the perovskite structure. The aging process conducted on LaCo . – Fe Pd . O was carried out by thermally treating the catalysts in air at 1223 K for 6 h.

Product Characterization

The crystal structures of the as-prepared catalysts were characterized by XRD using a D8 Advance diffractometer (Cu-K radiation) operated at 40 kV and 40 mA at a step of 0.02°s^{1} with the Bragg angle (2) ranging from 10 to 90°. The morphologies of the catalysts were analyzed by TEM using a Tecnai F20 (FEI) instrument operated at 200 kV. The distribution of palladium was determined by field-emission scanning electron microscopy (FESEM) in combination with energy dispersive spectrometry (EDS) mapping (S-4800, Hitachi). The specific surface areas (SSA) of the catalysts were measured by means of the Brunauer-Emmett-Teller (BET) isotherm technique with nitrogen adsorption (V-sorb 2800P, China). The samples were degassed at 473 K for 2 h prior to analysis.

The valence states of the surface ions were determined by XPS using an AXIS ULTRADLD multifunctional X-ray photoelectron spectroscope (Al-K radiation) operating at room temperature and under a vacuum of 10 Pa (10 Torr) with the starting angle of the photoelectron set at 90°. H TPR measurements were performed with a FINESORB3010 instrument (Zhejiang Finetec Co.) equipped with a thermal conductivity detector (TCD) with the sample (30 mg) loaded into the U-type quartz tube reactor for each test. Prior to reduction, the samples were pretreated at 573 K for 30 min with a stream of 21% O /N (70 mL/min) and then cooled to room temperature under the same atmosphere and subsequently purged with a 10% H /Ar mixture (50 mL min^{1}) for 30 min. Then the samples were kept in the 10% H /Ar mixture (50 mL min^{1}) at the same temperature for a further 30 min to make sure the signal of TCD was stable. Then the temperature was increased from room temperature to 1073 K at a rate of 278 K min^{1} and kept at 1073 K for 30 min. The consumption of H was determined by using a TCD with Ar as the reference gas.

Evaluation of the Catalytic Activity

The catalytic activities of the compounds were measured by using the same reactor in temperature-programmed experiments, the reactor tube having a 3 mm internal diameter. For each test, 100 mg of catalyst was used and the temperature was measured by using a K-type thermocouple in direct contact with the upper quartz wool close to the sample. The temperature inside the reactor was increased at a rate of 275 K min^{1} from room temperature with a total feed flow rate of 100 mL min^{1} corresponding to a velocity of 60000 mL g^{1} h^{1}. The effluent gas was analyzed by using an FGA-4100 automotive emission analyzer (Foshan Analytical Instrument Co.). The experimental feed stream simulated the automotive exhaust gas composition with a theoretical air/fuel (A/F) ratio of 14.7 and was prepared by mixing appropriate amounts of gas (2.27 vol.-% CO, 13.60 vol.-% CO , 0.22732 vol.-% NO, and 0.05254 vol.-% C H , balanced with nitrogen, supplied by Dalian Special Gases Co.) and O (21 vol.-%, balanced with nitrogen). The conversions of X (CO, HC, NO) are defined as the percentage of X in the feed that has reacted and is given by Equation (1) in which X is the concentration of X in the inlet gas and X is the concentration of X in the outlet gas. The temperatures at which 50 and 90% conversion occur are denoted as T and T , respectively.

Conversion [%] = (X -X) / X × 100

Conclusions

The influence of Fe doping on the stability and catalytic performances of LaCoO -based three-way catalysts containing Pd, synthesized by a modified sol-gel method, has been systematically studied. The introduction of Fe at the B sites of the ABO perovskite structure inhibits the reduction of Co^{2} to Co without affecting the reduction of Co^{3} to Co^{2}, thereby enhancing the thermostability of the Pd-containing LaCoO perovskite structure. Moreover, the catalytic performances of the Fe-doped catalysts are also improved in comparison with the Fe-free catalyst due to an increase in the amount of Pd at the surface. After aging the catalysts at 1223 K in air, the Pd component in all the samples disappeared and only the Pd^{2} component was observed whereas the perovskite bulk phase became more pure, resulting in similar catalytic performances of the as-prepared catalysts. However, the catalytic properties of the Fe-doped samples are still superior to those of the Fe-free catalyst due to the better reducing properties of the former. Thus, this approach has proved to be a useful method for investigating potential materials for the treatment of exhaust emissions from gasoline vehicles.

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