Improved Intrinsic Activity of Ce$_{0.5}$Pr$_{0.5}$O$_2$ for Soot Combustion by Vacuum/Freeze-Drying

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Vacuum-drying and freeze-drying were adopted to improve the catalytic activity of Ce$_{0.5}$Pr$_{0.5}$O$_2$ for soot combustion. The specific surface area and pore volume of the as-prepared Ce$_{0.5}$Pr$_{0.5}$O$_2$ were greatly increased compared to the counterpart using the common drying method. Furthermore, the redox performance and the oxidation ability for soot were enhanced, as demonstrated by H$_2$-TPR and soot-TPR. Thus, lower combustion temperatures and higher intrinsic activity were obtained. This work demonstrated that simply changing the drying process of precipitates can be served as a paradigm to improve the structure and catalytic performance.

Keywords: soot oxidation, Ce$_{0.5}$Pr$_{0.5}$O$_2$, vacuum-drying, freeze-drying, intrinsic activity

INTRODUCTION

Soot particulates emitted from diesel engines have caused seriously deleterious effects on human health and environment (Wei et al., 2011; Lin et al., 2013; Wei et al., 2014; Fino et al., 2016; Yu et al., 2019; Tsai et al., 2020). The catalytic combustion technique combined with diesel particulate filters (DPFs) (Kumar et al., 2012; Feng et al., 2016; Cheng et al., 2017; Ren et al., 2019; Fang et al., 2020; Jin et al., 2020; Zhao et al., 2020) has been considered as one of the most efficient ways to eliminate soot, of which the key point is to explore a highly active catalyst.

CeO$_2$ has been extensively used as an excellent catalyst for soot combustion due to its remarkable oxygen storage capacity (OSC) and redox property (Piumetti et al., 2015). Doping with metal ions can further improve its catalytic performance (Liu et al., 2008; Fu et al., 2010; Muroyama et al., 2010; Zhang et al., 2010; Li et al., 2011; Lim et al., 2011; Wang et al., 2015; Lin et al., 2018; Yang et al., 2019; Cui et al., 2020). In particular, doping of rare earth elements can induce distortion of the CeO$_2$ lattice, leading to the formation of more oxygen vacancies, thereby improving the oxygen storage/release property and redox capability (Aneggi et al., 2012). Bueno-López et al. (Bueno-López, 2014) reported that doping of La$^{3+}$ increases surface area and redox properties of CeO$_2$, and thus enhances its catalytic soot combustion activity. Hernández-Giménez et al. (Hernández-Giménez et al., 2013) found that by doping of Nd, the soot combustion activity of Ce-Zr mixed oxide can be improved. Impressively, Pr-doped CeO$_2$ was shown to be more active than other Ce-based oxides (Krishna et al., 2007; Bueno-López, 2014; Guillaud-Hurtado et al., 2015). Therein, Ce$_{0.5}$Pr$_{0.5}$O$_2$ with the highest surface area and smallest particle size is even better than a reference Pt-based commercial catalyst (Guillaud-Hurtado et al., 2015). The enhancement of Pr and La doping for soot combustion was attributed to the increased lattice oxygen activity (Harada et al., 2014).

So far, coprecipitation (Katta et al., 2010; Kumar et al., 2012; Venkataswamy et al., 2014; Muroyama et al., 2015; Devaiah et al., 2016), hydrothermal (Nakagawa et al., 2015; Piumetti et al., 2015), sol–gel (Oliveira et al., 2012; Zhou et al., 2015; Alcalde-Santiago et al., 2019), microemulsion
(Fan et al., 2017), and solid-phase grinding have been used to prepare CeO$_2$-based oxides. However, the drying methods are scarcely discussed. Generally, improving the drying process can decrease the agglomeration of catalyst particles and have a positive impact on catalytic activity (Fan et al., 2014). In this work, vacuum-drying and direct freeze-drying were adopted to coprecipitated Ce$_{0.5}$Pr$_{0.5}$O$_2$ and compared with the common drying method. XRD, BET, H$_2$-TPR, and soot-TPR were used to characterize the physiochemical properties of the as-prepared catalysts so that the effects of drying treatment on the catalytic soot combustion performance can be deduced.

**EXPERIMENTAL**

**Catalyst Preparation**

1.2593 g of Ce(NO$_3$)$_3$·6H$_2$O and 1.2593 g of Pr(NO$_3$)$_3$·6H$_2$O were dissolved in 10 ml deionized water at room temperature. NH$_3$·H$_2$O was added dropwise under vigorous stirring until the pH reached ∼9. Then, the precipitates were kept at room temperature for 24 h, followed by filtration and washing with deionized water until a pH of 7 was attained. After that, the precipitates were dried at 100°C for 12 h and finally calcined at 500°C for 2 h in the muffle furnace with the heating rate of 1°C/min. The sample obtained is denoted as CPO.

Based on the above method, the drying process was improved. For vacuum-drying, the precipitate was immersed in 250 ml of ethanol for 24 h under static conditions for the sake of substituting water with ethanol. Subsequently, the precipitate was filtered to remove alcohol and then dried at 80°C for 12 h in a vacuum oven. Finally, the sample was calcined at 500°C for 2 h in the muffle furnace with a heating rate of 1°C/min. The sample obtained is denoted as CPO-E. For freeze-drying, the precipitate was placed in a freeze dryer and dried for 24 h. Finally, the sample was calcined at 500°C for 2 h in the muffle furnace with a heating rate of 1°C/min. The sample obtained is denoted as CPO-F.

**Characterizations**

X-ray powder diffraction (XRD) patterns were measured on a D8FOCUS powder X-ray diffraction instrument (Bruker AXS, Germany) using 40 kV as tube voltage and 40 mA as tube current.

Surface area and pore size distribution were determined by N$_2$ adsorption/desorption at 77 K using the Brunauer–Emmett–Teller (BET) method with a Micromeritics ASAP 2020 instrument after out-gassing for 5 h at 300°C prior to analysis.

Temperature-programmed reduction with H$_2$ (H$_2$-TPR) experiments were performed in a quartz reactor with a thermal conductivity detector (TCD) to monitor H$_2$ consumption. A 50 mg sample was pretreated *in situ* for 30 min at 200°C in a flow of O$_2$ (30 ml/min) and cooled to room temperature in the presence of O$_2$. After purging in N$_2$, TPR was conducted at 10°C/min up to 900°C in a 30 ml/min flow of 5 vol.% H$_2$ in N$_2$. To quantify the total amount of H$_2$ consumption, CuO was used as a calibration reference.

Soot temperature–programmed reduction (soot-TPR) experiments were performed in a quartz reactor consistent with the activity test dosage. 50 mg sample of the soot–catalyst mixture and 100 mg of
quartz sand were pretreated in a flow of He (100 ml/min) at 200°C for 30 min to remove adsorbed species. After cooling to room temperature, the temperature was also programmed in a He atmosphere under the condition of a heating rate of 5°C/min, reaching 850°C. CO2 during the reaction was detected by mass spectrometry (MS, OminiStar 200, Balzers).

**Catalytic Activity**

Temperature-programmed oxidation (TPO) reactions were conducted in a fixed bed micro-reactor. Printex-U from Degussa is used as the model soot. Two conditions (tight and loose contact) were employed in this study, in which 45 mg of catalyst and 5 mg of soot were used. In tight contact conditions, soot was mixed with the catalyst in an agate mortar for 30 min to obtain a homogeneous mixture. In loose contact conditions, the catalyst–soot mixture was added into a small flask and shaken for 24 h. 50 mg sample of the soot–catalyst mixture was pretreated in a flow of He (100 ml/min) at 200°C for 30 min to remove adsorbed species. After cooling to room temperature, a gas flow with 5 vol.% O2 in He was introduced, and then TPO was started at a heating rate of 5°C/min until reaching 750°C. The effluent gases were monitored online using a gas chromatograph (GC, SP-6890, Shandong Lunan Ruihong Chemical Instrument Corporation, China) fitted with a methanator. The activity for soot combustion was evaluated by $T_m$, the temperature corresponding to the maximum soot combustion rate. The selectivity to CO2 ($S_{CO2}$) is defined as the percentage CO2 in the outlet concentration divided by the sum of the CO2 and CO outlet concentrations.

The intrinsic activity, turnover frequency (TOF), is measured by an isothermal anaerobic titration with soot as a probe molecule, as suggested by us previously (Zhang et al., 2010). A 50 mg mixture of catalyst and soot (9:1) below 300 mesh was diluted with 100 mg silica (below 300 mesh). After pretreatment in a flow of He (100 ml/min) at 120 °C for 20 min, a gas flow with 5 vol.% O2 in He (200 ml/min) was introduced. The isothermal reaction rates were detected at 280°C when the soot conversion is stable and low but sufficient for analysis purposes. When comparable soot conversions were reached for all the samples, O2 was replaced with He. The transient decay in concentrations from the steady state was monitored using a gas chromatograph. The number of active redox sites available to soot under these reaction conditions can be quantified by integrating the diminishing rate of CO2 formation over time.

### RESULTS AND DISCUSSION

XRD patterns show that all the as-prepared samples are indexed to the structure of fluorite CeO2 (JCPDS 43–1002), and no other

| TABLE 1 | Texture properties, hydrogen consumption, and catalytic soot oxidation activity of samples. |
| Samples      | Surface area (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | H₂-TPR | $T_m$ (°C) | $S_{CO2}$ (%) | Rate (μmol·s⁻¹·g⁻¹) | TOF (s⁻¹×10⁻⁵) |
|--------------|------------------------|----------------------|--------|------------|--------------|---------------------|----------------|
| CPO          | 51                     | 0.096                | 410    | 2952.5     | 400° (514°)  | 93.62               | 0.044          | 0.426          |
| CPO-E        | 95                     | 0.324                | 406    | 3284.8     | 390° (492°)  | 94.73               | 0.091          | 0.581          |
| CPO-F        | 93                     | 0.347                | 403    | 3826.2     | 389° (493°)  | 94.75               | 0.073          | 0.546          |

*aUnder tight contact conditions.

*bUnder loose contact conditions.

![H₂-TPR curves of CPO, CPO-E, and CPO-F.](image)

![Soot-TPR and initial soot consumption rate (inset) curves of CPO, CPO-E, and CPO-F.](image)
peaks were found (Figure 1), implying the formation of CePr solid solution due to the similar ionic radius of Ce$^{4+}$ (0.97 Å) with Pr$^{4+}$ (0.96 Å). This confirms that changing drying methods does not change the phase structure of the CePr composite oxides. Additionally, it is noted that the intensity of the diffraction peaks of CPO-E and CPO-F is lower than those of CPO, suggesting the lower crystallinity or more defects/vacancies for CPO-E and CPO-F, which would benefit the redox property and catalytic activity (Martínez-Munuera et al., 2019).

Figure 2 shows $N_2$ adsorption/desorption isotherms and pore distribution curves. The type II isotherms with a type H3 hysteresis loop at relative pressure ($P/P_0$) range of $\sim$0.4–1.0 are observed (Figure 2A), indicating aggregates of plate-like particles with slit-shaped pores (Aneggi et al., 2012; Fan et al., 2014). Furthermore, both mesopores and macropores are detected (Figure 2B). However, the pore size distribution with a shift to lower values was observed for CPO-E and CPO-F compared with CPO, while the BET surface areas of CPO-E and CPO-F are nearly double that of CPO, and pore volumes more than triple (Table 1), confirming the looser texture and abundant pores for the former two samples derived from the vacuum- and freeze-drying processes. This is possibly due to the loosely aggregated morphology under vacuum/freeze-drying process resulting in the elimination of surface tension effects.

The redox properties of the catalysts were investigated by H$_2$-TPR. As shown in Figure 3, two H$_2$ consumption peaks, a prominent one with a should and a small one above 500°C, were observed, which can be attributed to the reduction of surface and subsurface Ce$^{4+}$ and Pr$^{4+}$ reduction (Krishna et al., 2007; Guillén-Hurtado et al., 2015). Importantly, the first peak appears earlier for CPO-E and CPO-F than for CPO, indicating the higher reducibility of CePr oxide solid solutions using vacuum/freeze-drying methods. Furthermore, the H$_2$ amounts consumed for CPO-E and CPO-F were much higher than those consumed for CPO (Table 1), suggesting that not only the reactivity of active oxygen but also the amount involved are improved.

To be more realistic, soot was used as a probe agent for TPR reactions (Figure 4). Similar with H$_2$-TPR, two CO$_2$ production peaks are observed. Furthermore, the lower temperature of the first reduction peaks for CPO-E and CPO-F in comparison with CPO confirmed the increase of surface lattice oxygen activity for soot combustion (Machida et al., 2008; Aneggi et al., 2012; Harada et al., 2014). On the other hand, the low-temperature reducibility of catalysts can be evaluated using the initial soot
consumption rates. The soot consumption rates of CPO-E and CPO-F are much higher than those of CPO, confirming the stronger ability of active oxygen species in CPO-E and CPO-F for oxidizing soot.

Figure 5 shows soot combustion conversion profiles under tight and loose contact conditions in O}_2 atmosphere. Both CPO-E and CPO-F show lower T_m and higher S_{CO2} than CPO in the tight contact conditions. For the sake of disclosing the differentiation in intrinsic activity, isothermal reactions at 280 °C and anaerobic titration tests were performed (Li et al., 2011; Zhang et al., 2010), from which the reaction rates, the amounts of active oxygen, and the TOF values can be obtained (Figure 6). As listed in Table 1, higher reaction rates and TOF values were achieved on CPO-E and CPO-F, which is consistent with the results of H_2-TPR (Figure 4) and soot-TPR (Figure 4). In the loose contact conditions, similar activity results were observed, but all T_m shift to higher temperatures than that in the tight contact conditions (Figure 5). Clearly, the activity improvement after vacuum-drying and freeze-drying is more evident, because the difference of T_m between CPO-E/CPO-F and CPO is 20 °C, while under the tight contact conditions, only 10 °C was detected (Table 1). This could be attributed to bigger pore volumes and surface areas of CPO-E and CPO-F (Table 1), improving soot dispersion on catalysts and thus the contact efficiency of soot with catalyst under loose contact conditions, as well as facilitating fast oxygen delivery (Martínez-Munuera et al., 2019).

CONCLUSION

Vacuum-drying and freeze-drying were used to improve the activity of Ce_{0.5}Pr_{0.5}O_2, a promising soot combustion catalyst.

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Lower crystallinity, higher surface area, larger pore volume, and stronger redox properties were obtained compared to the counterpart using the common drying method. Therefore, lower soot oxidation temperatures and higher intrinsic activity were achieved. It is a good paradigm for catalysts to enhance catalytic performance simply by changing drying methods during the preparation process.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

QL designed and performed experiments. YS prepared the samples used in this work. XL helped synthesizing catalysts. YL and NZ helped characterizing samples. QL, YX, and ZZ discussed the results. QL and ZZ wrote the manuscript and supervised the project.

FUNDING

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21876061 and 22076062), the Natural Science Foundation of Shandong Province (No. ZR2020MB090), and science and technology projects of the University of Jinan (No. XKY1905).

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