The effect of the decreased defect concentration in ceria by the thermal treatment prior to the Pt loading on the Pt-ceria interaction and the CO oxidation ability of Pt/CeO$_2$ catalysts

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Abstract: The CO oxidation ability can be modulated by controlling the metal-support interaction of Pt/CeO$_2$ catalysts. Pt/(800°C)CeO$_2$ prepared by the thermal treatment of ceria at 800 °C before loading Pt maintained the much higher Pt dispersion than Pt/γ-Al$_2$O$_3$ after the thermal aging at 800 °C. In addition, the light-off curve of the CO oxidation shifted to the lower temperature by more than 70 °C in Pt/(800°C)CeO$_2$ than in Pt/CeO$_2$ catalyst without the thermal treatment. Such enhanced activity is explained by the formation of PtO$_2$ species that interact weakly with ceria rather than Pt-O-Ce species interacting strongly with ceria.

Keywords: Metal-support interaction, Thermal treatment, Pt/CeO$_2$, CO oxidation

1. Introduction

It is well known that ceria could be used as a support for PGM based catalysts with high metal dispersion and enhanced thermal stability. Nagai et al. showed that the EXAFS analysis of Pt/CeO$_2$ treated at oxidative atmosphere provided the evidence about the formation of strong Pt-O-Ce bond, which prevents Pt agglomeration at elevated temperature (~800 °C) and maintains the high Pt dispersion in the wide temperature range [1]. We recently showed that the strong Pt-O-Ce bond enhances the thermal stability of ceria support as well as prevents Pt agglomeration [2]. In addition, when Pt species are coordinated to O via Pt-O-Ce bond, Pt species exist in 2+ state, according to X-ray photoelectron spectroscopy [2]. It means that Pt$^{2+}$ species in Pt-O-Ce bond plays a key role in preventing Pt sintering and ceria agglomeration.

The presence of Pt$^{2+}$ species in Pt-O-Ce bond could be beneficial in some reactions. For example, Pt$^{2+}$ is reported to be the active site for water-gas-shift reaction (WGSR) [3, 4]. Despite the important role of Pt$^{2+}$ species in preventing the Pt sintering and promoting WGSR, the presence of strong Pt-O-Ce bond could be unfavorable for oxidation reactions. Recently, Gatla et al. reported that the CO oxidation of Pt/CeO$_2$ was improved with the formation of elongated Pt-O-Ce bond, with O more loosely connecting Pt and Ce atoms [5]. The present work aims at investigating the influence of change in Pt-CeO$_2$ interaction on the CO oxidation ability and the Pt sintering behavior.

2. Experimental

Pt was loaded on ceria (Rhodia, 135 m$^2$/g) or alumina (Sasol, 250 m$^2$/g) by applying the incipient wetness impregnation method. Ceria was annealed at 800 °C in flowing 100 mL/min of 15% O$_2$/N$_2$ for 2 h prior to Pt impregnation to weaken the metal-support interaction. Catalysts were denoted as Pt(x)/CeO$_2$ or Pt(x)/γ-Al$_2$O$_3$ or Pt(x)/(800°C)CeO$_2$ where x is the wt% of Pt loaded on the catalyst. XRD patterns were taken in a Rigaku (mode 1 smartlab) diffractometer with Cu Kα radiation ($\lambda$=0.1542 nm). N$_2$ adsorption/desorption isotherms were measured on a Micromeritics ASAP 2010 apparatus. Static CO chemisorption was measured on a Micromeritics ASAP 2010. The Raman spectra were obtained from a BaySpecNomadic™ Raman spectrometer. XPS analysis was performed on the AXIS-HSi (Kratos) instrument. Cryo-H$_2$-temperature programmed reduction (Cryo-H$_2$-TPR) was performed using a BEL-CAT-II (BEL Japan Inc.) instrument. The CO oxidation ability of catalysts were measured in a fixed-bed quartz reactor. A 0.05 g of catalyst was mixed with 0.1 g of α-Al$_2$O$_3$ to dissipate the heat produced during the reaction. Temperature was increased from room temperature to 500 °C with the ramping rate of 4 °C/min.
3. Results and discussion

The interaction between Pt and CeO$_2$ was weakened by thermally treating ceria at 800 °C before loading Pt. Raman spectra showed that defect concentration on ceria surface decreased after the oxidative treatment at 800 °C. CO chemisorption curves and XP spectra showed that when the amount of Pt loaded exceed the amount of CO chemisorbed, Pt species free from Pt-O-Ce bond appeared on ceria in the form of Pt$^{4+}$ state. The CO oxidation ability of Pt/CeO$_2$ was greatly enhanced with the thermal treatment of ceria before Pt loading (Figure 1). Pt(2)/(800C)CeO$_2$ even showed the CO oxidation activity at room temperature. Kinetic study revealed that the weakened metal support interaction between Pt and (800C)CeO$_2$ lowered the CO oxidation activation energy, resulting in the improved CO oxidation ability compared with Pt/CeO$_2$ catalysts.

XRD pattern of Pt(2)/(800C)CeO$_2$ showed the appearance of small amount of Pt metal clusters (larger than 5 nm) after the oxidative treatment at 800 °C, which was not observed on Pt/CeO$_2$. This could be ascribed to the weakened interaction between Pt and ceria after the thermal treatment of ceria before loading Pt. However, CO chemisorption curves showed that relatively high Pt dispersion was still maintained on (800C)CeO$_2$, where the Pt dispersion of Pt(2)/(800C)CeO$_2$ was measured to be 47 % after the oxidative treatment at 800 °C. It seems that the remaining strong Pt-CeO$_2$ interaction on Pt/(800C)CeO$_2$ retained the high Pt dispersion. In the present work, Pt-CeO$_2$ interaction was weakened by the simple thermal treatment of ceria before loading Pt, and the CO oxidation ability of the resultant catalyst was greatly enhanced while retaining the excellent thermal resistance against Pt sintering.

![Figure 1](attachment:image.png)

**Figure 1.** (a) The temperature dependence of TOF of Pt(2)/CeO$_2$ 500C and 800C catalysts. (b) The temperature dependence of TOF of Pt(2)/(800C)CeO$_2$ 500C and 800C catalysts. For a comparison, TOFs of Pt(2)/γ-Al$_2$O$_3$ 500C are provided in the figure.

4. Conclusions

In the present work, the Pt-ceria interaction was impaired by impregnating Pt species onto the thermally treated ceria surface with reduced defect concentrations. Such treatment decreased the Pt-ceria interaction and the thermal stability of Pt atoms was slightly decreased. However, when the Pt-ceria interaction is weakened, the PtO$_2$ moieties were formed on the ceria surface to improve the CO oxidation ability, but the Pt dispersion remained relatively high even after the thermal treatment at 800 °C. This study shows that the attenuation of the metal-support interaction could be an attractive strategy for preparing the high performance catalyst.

References