

RKCL3650

CO AND METHANE OXIDATION OVER $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ MIXED OXIDE SUPPORTED PdO CATALYSTS

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Received May 22, 2000

Accepted June 13, 2000

Abstract

In this paper, the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ -supported PdO catalysts were prepared and the effect of Ce/Zr ratio on catalytic activity for CO and methane oxidation was studied, both activity and the reduction behavior of catalyst depend on the Ce/Zr ratio. The reduction behavior of those catalysts was characterized by means of TPR.

Keywords: CO oxidation, methane oxidation, PdO, $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ mixed oxides

INTRODUCTION

Volatile organic compounds (VOCs) and CO are recognized as major contributors to air pollution. Major emission sources are vehicles (car and trucks), and various industrial sites (such as plants, manufacturing organic chemicals, polymers, or synthetic, fibers, *etc.*). Catalytic combustion is one of the most important processes for VOCs and CO destruction. Cerium oxide has been widely used in the automotive three-way catalytic converter. The structural modification and imperfection of the CeO_2 lattice by insertion of other cation cause the enhancement of redox properties and oxidation activity in low-temperature of the CeO_2 catalyst. For example, $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x=0\sim 1$) mixed oxides has higher thermal stability, redox properties and catalytic activity than that of CeO_2 [1-3]. In this work, we report the activity of PdO/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x=0\sim 1$) catalysts for low-temperature CO and methane oxidation, and some interesting results obtained.

EXPERIMENTAL

Preparation of catalysts

$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ mixed oxides were prepared by the citrate sol-gel method [4]. An equivalent amount of citric acid was added into the mixed metal nitrate solution, then evaporated to gel at 95~100°C with stirring. The gel prepared was dried at 100°C, finally calcined at 950°C in air for 4 h to obtain a yellow powder.

The supported PdO catalysts were prepared by the conventional impregnation method using an aqueous solution of H_2PdCl_4 . Prepared samples were dried at 120°C, and then calcined at 650°C in air for 4 h. The loading of Pd is 0.25%. The catalysts are denoted as $\text{PdO/Ce}_x\text{Zr}_{1-x}\text{O}_2$.

Activity measurement for CO and methane oxidation

Catalytic activity measurement was carried out in a fixed bed reactor using 150 mg catalyst. The flow rate of the feed gas was 80 mL/min. The catalysts were directly exposed to the reaction gas as the reactor temperature was stabilized without any pretreatment. In CO oxidation, the gas consisted of 2.4% CO and 1.2% O_2 in N_2 . In methane oxidation, the gas consisted of 2.8% methane and 8% O_2 in N_2 . The analysis of the reactor effluent was performed with on an on-line SP-2304 model gas chromatograph with a TCD. The chromatographic columns were 13X molecular sieve and Propark Q.

H_2 -temperature programmed reduction (H_2 -TPR)

TPR measurements were made in a flow system. 25 mg catalyst was placed in a TPR cell (6 mm i.d.), into which H_2 - N_2 (5:95) mixed gas was introduced. The temperature of the sample was programmed to rise at a constant rate of 20°C/min and the amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD). The water produced in TPR was trapped on a 5 Å molecular sieve.

RESULTS AND DISCUSSION

Catalytic activity for CO and methane oxidation

Figure 1 shows the catalytic activity of a series of $\text{PdO/Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x=0\sim1$) catalysts for CO oxidation. The catalytic activity was compared on the basis of

T_{20} and T_{90} (the temperatures at 20% and 90% conversion), respectively. From Fig. 1, it can be observed that the CO oxidation on PdO/CeO₂ catalyst is faster than that on PdO/ZrO₂. The catalytic activity has a maximum and a minimum with increasing the x value from 0.1 to 0.9. Namely, the PdO/Ce_{0.8}Zr_{0.2}O₂ catalyst exhibits the highest activity in the series catalysts, its T_{90} is only 110°C, while the PdO/Ce_{0.2}Zr_{0.8}O₂ catalyst exhibits the lowest activity. This indicates that a small amount of cerium inhibits the catalytic activity for CO oxidation. Then the oxidation activity of PdO/Ce _{x} Zr_{1- x} O₂ catalysts is enhanced by further increase of the content of cerium ($x=0.3\sim 0.8$). The catalytic activity decreases remarkably with increasing x value from 0.9 to 1.0.

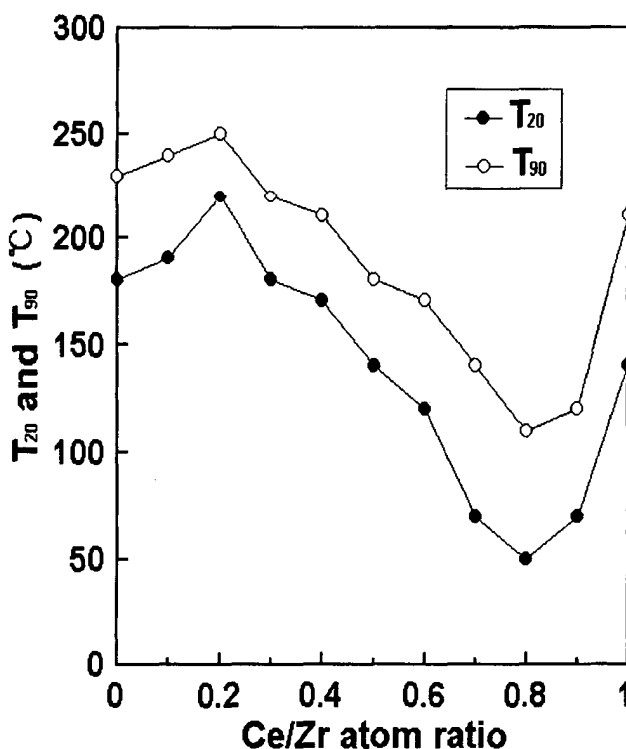


Fig. 1. Activity of PdO/Ce _{x} Zr_{1- x} O₂ catalysts for CO oxidation

Figure 2 shows the catalytic activity of PdO/Ce _{x} Zr_{1- x} O₂ ($x=0\sim 1$) catalysts for methane oxidation. From Fig. 2, it can be seen that PdO/ZrO₂ for methane oxidation is more active than PdO/CeO₂. The activity of PdO/Ce_{0.1}Zr_{0.9}O₂

catalyst is similar to that of PdO/ZrO_2 . However, the activity of $\text{PdO}/\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ catalyst decreases remarkably. As the content of cerium increase again ($x=0.3\sim 1.0$), the activity of $\text{PdO}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyst shows a maximum. The $\text{PdO}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst is the most active for methane oxidation in all catalysts.

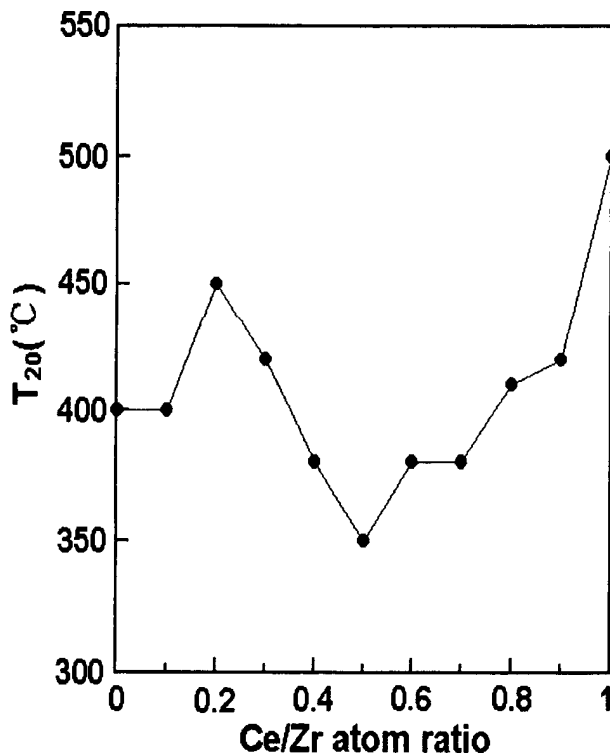


Fig. 2. Activity of $\text{PdO}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts for CH_4 oxidation

Temperature-programmed reduction

Figure 3 shows the TPR profile of $\text{PdO}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x=0\sim 1$) catalysts. According to our previous work [5], we believe that the low temperature reduction peak (α) may be attributed to the reduction of PdO . The temperature of α peak is almost the same in all catalysts except for that of the $\text{PdO}/\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ catalyst which obviously shifts to higher temperature. For the

PdO/CeO₂ catalyst, only one peak(γ) is observed at about 850°C besides the α peak. For PdO/Ce_xZr_{1-x}O₂ ($x=0.2\sim0.9$) catalysts, an overlap peak (β_1 and β_2) is observed from 150 to 500°C. As x increases, β_1 and β_2 overlap much more obviously, and shift to lower temperature. We believe that the $\beta(\beta_1 + \beta_2)$ reduction peaks may be attributed to the reduction of Ce_xZr_{1-x}O₂ support. When $x=0.8$ and 0.9 , α and β peaks overlap obviously, and a new peak (γ) at high temperature ($\sim 750^\circ\text{C}$) is observed. Comparing with the PdO/CeO₂ catalyst, we assume that the Ce-Zr mixed oxide may have two reduction species in the PdO/Ce_{0.8}Zr_{0.2}O₂ and PdO/Ce_{0.9}Zr_{0.1}O₂ catalysts. One is Ce-Zr mixed oxide which strongly interacts with PdO, the other weakly interacts with PdO. The former is easy to reduce because it readily accepts H atom spillover from Pd, while the latter behaves in an opposite way. We found that the activity for CO oxidation was in accord with the α peak area, so that is thought to be the active species for CO oxidation. The activity for methane oxidation is in accord with the area of the β peak, so the β peak is believed to be the active species for methane oxidation. The catalytic activity of the PdO/Ce_{0.2}Zr_{0.8}O₂ catalyst is lower than that of PdO/ZrO₂ and its α peak shifts to higher temperature obviously. This may be related to the structure of the Ce_{0.2}Zr_{0.8}O₂ mixed oxide, because its phase structure is tetragonal, but that of ZrO₂ is monoclinic [4]. On the basis of the results mentioned above, we believe that the ratio of Ce/Zr effects on the catalytic activity of PdO/Ce_xZr_{1-x}O₂ catalyst remarkably.

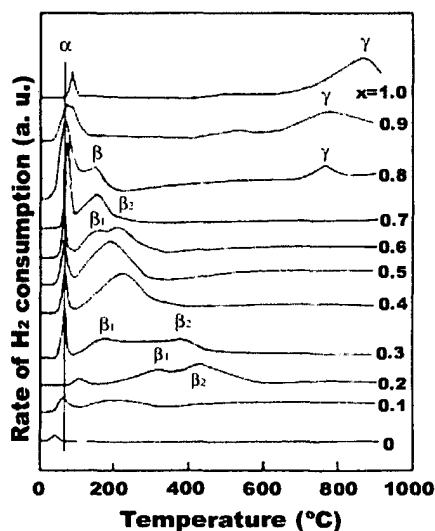


Fig. 3. H₂-TPR profiles of PdO/Ce_xZr_{1-x}O₂ catalysts

Conclusively, the ratio of Ce/Zr affects the activity of $\text{PdO/Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts remarkably. $\text{PdO/Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalyst is the most active for the CO oxidation, while the $\text{PdO/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst is the most active for methane oxidation. The lower temperature peak (α) is believed to be the active species for CO oxidation and the higher temperature peak (β) is believed to be the active species for methane oxidation.

Acknowledgment. This research project was supported by the Zhejiang Provincial Natural Science Foundation of China.

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