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The Support Effect on PdO/$Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ and CuO/$Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ Catalysts[1]

Min Chen, Lingyan Qi, and Xiaoming Zheng
Institute of Catalysis, Zhejiang University, Xixi Campus, Hangzhou, P.R. China
e-mail: chenmin@zju.edu.cn

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Abstract—$Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxides (denoted as CZB) were prepared using macromolecule surface modified methods and used as supports to prepare low palladium content of PdO/CZB model catalysts. CuO/CZB series of catalysts were also prepared for comparison. The catalytic activity of the PdOCZB and CuO/CZB series of catalysts for low-temperature CO oxidation was investigated. A significant influence of the $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ support on the catalytic performance has been found. Using $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ as catalyst support increased the activity of CO oxidation and promoted the thermal stability significantly. It was found that the transition metal supported catalyst of 10.0 wt % CuO/CZB obtained a good result, as did the precious metal supported catalysts of 0.75 wt % PdO/CZB. The catalytic behaviors and thermal stability of PdO/CZB and CuO/CZB catalysts greatly depended on the support effect. The nature of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ support was also characterized by surface area (BET method), x-ray powder diffraction (XRD), transmission electron microscopy (TEM), temperature programmed reduction with hydrogen (H_2-TPR) and X-ray photoelectron spectroscopy (XPS) technologies.

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1. INTRODUCTION

The damage of waste gases such as CO, HC, and NO_x has caused many environmental problems due to their toxic or photochemical properties. Among the methods applied to remove CO, HC, and NO_x, catalytic oxidation is an efficient way to convert CO to CO_2 at low temperature. There are many reports about precious metal catalysts and transition metals catalysts, such as palladium and copper oxide as active compounds. They are preferred for CO oxidation due to their high activity [1–3]. However, thermal stability is a major disadvantage for the supported catalyst used in the oxidation reaction. Due to the severe operating conditions, the majority catalysts and supports show low thermal resistance [4]. Furthermore, it is difficult to keep the high dispersion state of PdO and CuO particles on the support after high temperature calcinations [5]. To overcome these problems, attention has been focused on developing catalysts that are less expensive and that have more thermal stability than the materials presently in use.

In recent years, the use of ceria-based materials such as CeO_2–ZrO_2 mixed oxide in catalytic science has been well established. Undoubtedly, it has been used widely for its high thermal stability and redox properties that are better than single CeO_2 [6–9]. Terribile et al. reported that CeO_2–ZrO_2 mixed oxide with high surface areas of 230 m^2/g was obtained after calcination of 450°C, due to the use of a surfactant-assisted approach as a prepared method, but it drops to 40 m^2/g at the following treatment temperature of 800°C [10]. Several research groups have studied the application of Ba oxides as suitable components in oxidation catalysts: Piacentini et al. [11] investigated the relative abundance and thermal stability of Ba-containing species depending on their interaction with the Al_2O_3-support. Peralta et al. [12] studied the stability of Ba/CeO_2 catalysts and found this catalyst to be very active for soot combustion. Nevertheless, little attention has been paid to investigating nanosized $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide as catalyst support for the CO oxidation. This work is specifically focused on the preparation of nanosized $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide as catalyst support, and then supported PdO and CuO. Taking those corresponding catalysts for the total oxidation of CO, the support effect on the CO oxidation reaction was discussed.

2. EXPERIMENTAL

2.1. Sample Preparation

The macromolecule surface modified method (denoted as MSM method in the following) was used to prepare $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide powder. The mixing solutions of $Ce(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 4H_2O$, $Ba(NO_3)_3 \cdot 6H_2O$ were added respectively in a given amount, which depended on the designed composition of the mixed oxide. At room temperature, under vigorous stirring, the mixed solutions were added dropwise into a vigorously stirred solution of 5.0 wt % polyeth-

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[1] This article was submitted by the authors in English.

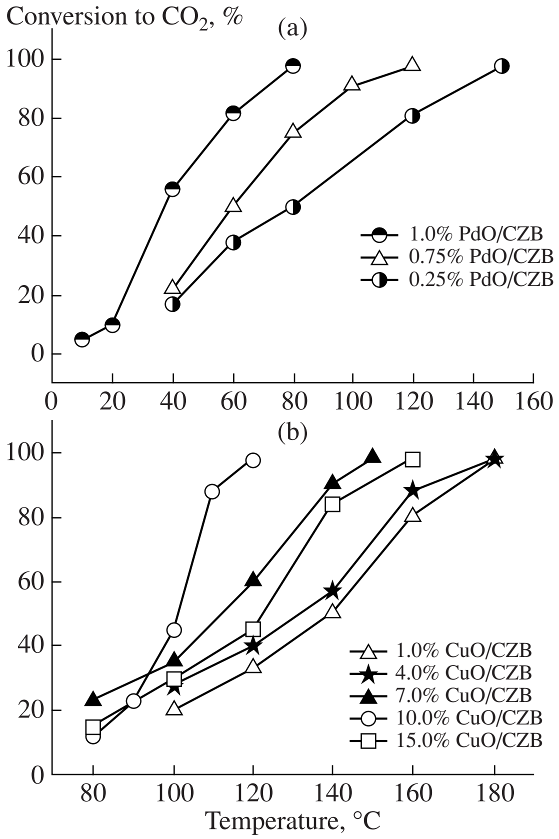

Fig. 1. (a) The CO oxidation activity of PdO/CZB catalysts with various PdO loading. (b) The CO oxidation activity of CuO/CZB catalysts with various CuO loading.

ylene glycol-20000, until the pH reached 9.0. The resulting suspension was frozen at low temperature (0°C) for 24 h. Then *n*-butyl alcohol was slowly added into the resulting gel and distilled at 120°C for 30 min. After repeated washings with distilled water, the gel was dried at 120°C for 2 h and then calcined at 600°C in air for 4 h. The synthesized $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ mixed oxide powder will be denoted as CZB in this paper.

The supported palladium catalyst on CZB was prepared by the conventional wet impregnation method. The content of PdO was 0.26, 0.75, and 1.0 wt %, respectively. The samples of palladium supported on CZB were calcined at 500°C for 4 h in air. They are referred to as PdO (wt %)/CZB, respectively in this paper. The preparation of CuO/CZB catalysts was the same. The content of CuO was 1.0, 4.0, 7.0, 10.0, and 15.0 wt %, respectively.

2.2. *Characterization Techniques*

The catalytic activity was tested using a fixed-bed flow type reactor (0.6 cm i.d.). A 150 mg catalyst was used, and the reaction gases for CO oxidation consisted of 5.0% CO, 3.6% O_2 in N_2. The analysis of the reactor effluent was performed on a chromatograph with a TCD attachment. The temperature at which CO conversion reaches 98%, as expressed by T_{98}, characterized the activity of the catalyst. The higher activity is indicated by a lower value of T_{98}.

The BET specific surface areas were determined by N_2 adsorption at 77 K on an OMNISORP 100CX instrument. The structure of the sample was assigned on the basis of XRD. The patterns were collected on a Rigaku D/max-IIIB instrument using a CuK_α radiation (40 kV and 40 mA). The particle size and dispersion state of PdO and CuO particles were determined by use of TEM with a JEM-200CX model microscope. TPR measurement was performed on a flow system with a thermal conductivity detector (TCD), and the carrier gas was a H_2–N_2 (5 : 95) mixture. Then, 10 mg of catalyst was used and the heating rate of the TPR was 20 K/min. XPS spectra were obtained using a PHI-550 model ESCA/SAM system. The binding energy was adjusted to the C1*s* peak at 284.6 eV, which existed in all measurements.

3. RESULTS AND DISCUSSION

3.1. *Catalytic Activity and Thermal Stability*

Figure 1a shows the CO oxidation activities of PdO/CZB catalysts with different PdO contents. None of these catalysts were pretreated before the reaction. The reaction was kept at each temperature point for about 0.5 h to achieve steady activity. It was found that the catalytic activity was increased upon PdO loading. A maximum CO conversion at 80, 110, and 150°C lower temperature was obtained on 1.0 wt % PdO/CZB, 0.75 wt % PdO/CZB, and 0.25 wt % PdO/CZB catalysts. In the case of CuO/CZB catalysts with different CuO loading, as shown in Fig. 1b, better performance was observed for the catalysts with 7.0, 10.0, and 15.0 wt % of CuO content. Furthermore, it was noted that the 10.0 wt % CuO/CZB catalyst is found to have the highest activity for CO oxidation, and it showed equal activity as compared to the 0.75 wt % PdO/CZB catalyst. In general, the precious metal supported catalysts presented higher catalytic activity than transition metal supported catalyst. It must be emphasized here that 10.0 wt % CuO/CZB catalysts can obtain a similar result to those obtained in 0.75 wt % PdO/CZB catalysts. In our opinion, it must be related to the support effect of the strong interaction of PdO and CuO with CZB. Additionally, it was found that when the content of CuO is higher than 10%, the catalytic activity decreases. This implies that the limit value of CuO on the CZB support is at 10.0 wt %, and then excess copper forms bulk CuO particles and contributes little to CO oxidation [13].

Furthermore, to study the thermal stability of PdO/CZB at different temperatures (500–1000°C), the lowest PdO content sample of 0.25 wt % PdO/CZB was investigated. Figure 2a indicates that the 0.25 wt % PdO/CZB catalyst shows very high and stable activity

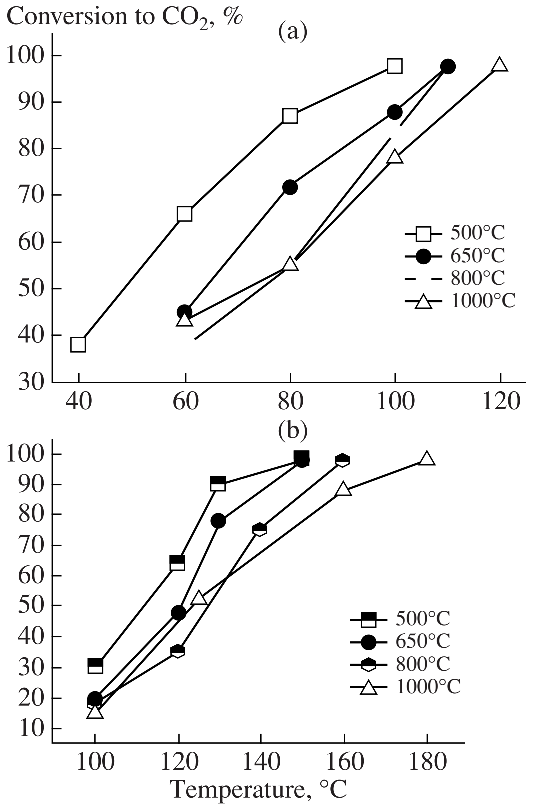

Fig. 2. (a) The CO oxidation activity of 0.25 wt % PdO/CZB at various calcination temperatures. (b) The CO oxidation activity of 10.0 wt % CuO/CZB at various calcination temperatures.

for the total CO oxidation, even for the catalyst after calcination at 1000°C. The conversion of CO is up to 98% at a much lower temperature of 120°C. In light of the optimistic results indicated in Fig. 1b, 10.0 wt % CuO/CZB was also selected in the following investigation for thermal stability measurement. As indicated in Fig. 2b, in the 10.0 wt % CuO/CZB catalyst, with the increasing of calcination temperature from 500 to 1000°C, the T_{98} values of the samples changed less when decreased from 150°C to 180°C, respectively. Hence, with regard to the temperature resistance of 0.25 wt % PdO/CZB and 10.0 wt % CuO/CZB, it shows that the thermal stability of the two catalysts should be related to the CZB support (which will be discussed in the following XRD result).

For comparison, the catalytic activity of CZB as a function of different preparation methods was also investigated. The sample of CZB prepared by the MSM method has a higher catalytic activity than the sample prepared by the sol-gel method. However, it is very interesting to find that the T_{98} of the sample prepared by MSM method is at 300°C, 120°C lower than those prepared by the sol-gel method [14]. On the other hand, another important observation was that the T_{98} value at the sample of CZB was 260°C and lower than that of $Ce_{0.75}Zr_{0.25}O_2$. It is clear that the support effect becomes more significant.

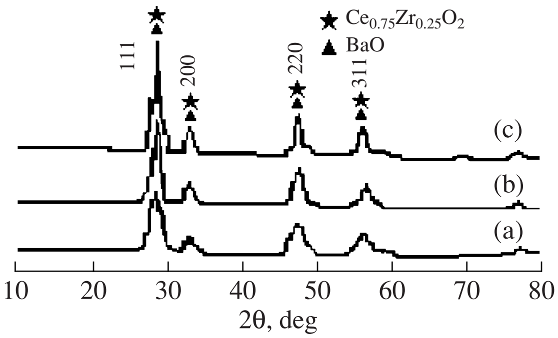

Fig. 3. XRD patterns of the $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_x$ samples calcined at different temperatures. (a) 600°C calcination; (b) 800°C calcination; (c) 1000°C calcination.

The following investigations were carried out to explain the reasons for CZB as catalyst support in its stability. In general, it is hard to avoid the decrease of the catalysts in its surface area after high temperature treatment; the nanosized material usually has a lower thermal stability than those of mixed oxide materials due to their particle size, which is easy to agglomeration. The surface areas of CZB and $Ce_{0.75}Zr_{0.25}O_2$ at various calcination temperatures are presented in Table 1. As shown in Table 1, the surface area decreased with increasing the temperatures. But, it must be emphasized here that the CZB sample offers a surface area nearly three times larger than that of $Ce_{0.75}Zr_{0.25}O_2$ when the calcination temperature increased from 600 to 1000°C. According to the above result, for the sample of CZB, it can be seen that CZB have much higher thermal stability than $Ce_{0.75}Zr_{0.25}O_2$.

3.2. XRD Measurements

Figure 3 shows the XRD patterns of CZB after calcination at 600, 800, and 1000°C for 4 h. From the XRD peaks, contrasted with the *JCPDS*, the diffraction peaks corresponding to $Ce_{0.75}Zr_{0.25}O_2$ and the BaO crystal phase can be observed in the sample of 600°C calcinations, and no visible peak due to the cerium, zirconium, and barium oxide crystal phase is observed. The intensity and half-width of XRD patterns shows no change in the other two samples when the calcination temperature increases from 600°C up to 800°C and

Table 1. BET surface areas of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ and $Ce_{0.75}Zr_{0.25}O_2$ at various calcination temperatures

Catalyst	Surface area, m^2/g		
	600°C calcination	800°C calcination	1000°C calcination
$Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$	119.0	87.4	23.3
$Ce_{0.75}Zr_{0.25}O_2$	39.3	35.4	8.6

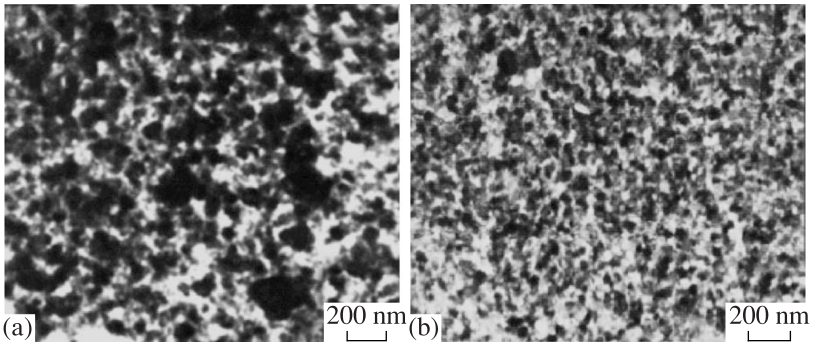

Fig. 4. TEM image of PdO/CZB and CuO/CZB of 500°C calcination; (a) PdO/CZB; (b) CuO/CZB.

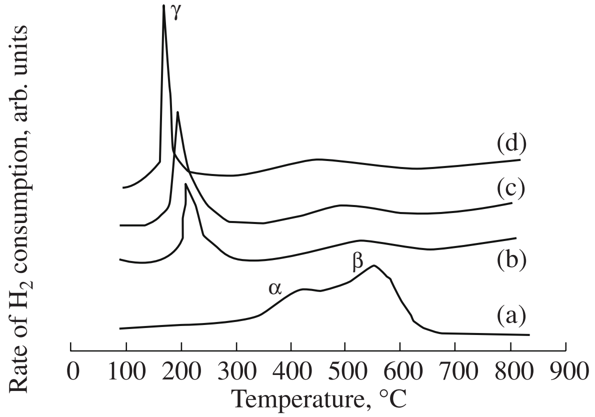

Fig. 5. TPR profile of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ and PdO/CZB catalysts. (a) $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$; (b) 0.25 wt % PdO/CZB; (c) 0.50 wt % PdO/CZB; (d) 1.0 wt % PdO/CZB.

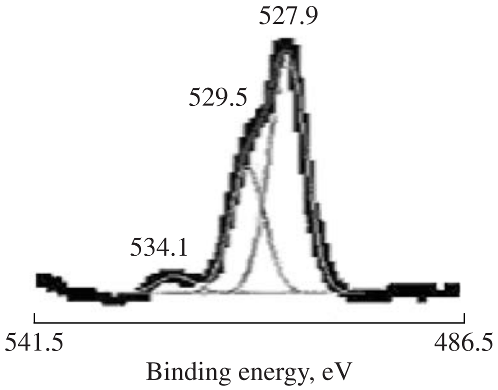

Fig. 6. O1s spectra of 0.25 wt % PdO/CZB catalyst.

1000°C. It shows high temperature calcination does not affect the structure of CZB support. We calculated the average particle size of samples (*a*), (*b*), (*c*) from the half-width of the 111, 200, 220, and 311 diffraction peak by use of the Scherrer formula [15]. It was found that they were all kept constant at 25, 34, and 56 nm even after 1000°C temperature, indicating the addition of barium was also effective in retarding the agglomeration of the particle size in ceria–zirconium mixed oxide at high temperatures.

Furthermore, the unit-cell parameters of $Ce_{0.75}Zr_{0.25}O_2$ mixed oxide was obtained from the XRD analysis. It can be seen that the planes (1 1 1), (2 0 0), (2 2 0), and (3 1 1) exhibit superimposed peaks, respectively. $Ce_{0.75}Zr_{0.25}O_2$ and BaO phases were too close to be superimposed in the crystal structure (unit-cell parameter of $Ce_{0.75}Zr_{0.25}O_2$ was 5.349 Å and that of BaO was 5.335 Å). These typical superposition phases of $Ce_{0.75}Zr_{0.25}O_2$ and BaO play a crucial role because isomorphic compounds can promote the dispersion of Ce–Zr and Ba^{2+} crystallite in Ce–Zr–Ba material [16]. This demonstrated that the addition of barium noticeably influenced the structure of ceria–zirconium mixed oxide. Clearly, the typical structure of superposition phases of $Ce_{0.75}Zr_{0.25}O_2$ and BaO seems to be responsible for enhancing the surface area of CZB support.

3.3. Textural and Structural Characterization

The TEM images of 0.75 wt % PdO/CZB and 10.0 wt % CuO/CZB catalysts calcined at 500°C are shown in Fig. 4. As can be observed, there is a good dispersion of palladium or palladium oxide (copper or copper oxide), giving a tightness contact with the support. All the active compounds of PdO and CuO are nanometer-sized in their particles; among them, PdO has a larger particle size of about 80–100 nm in PdO/CZB (Fig. 4a) and the size of CuO particles is about 60–80 nm in CuO/CZB (Fig. 4b). The good existence of nanosized PdO and CuO species should therefore favor the activity of PdO/CZB and CuO/CZB catalysts. Thus, it was found that CZB are an effective support for stabilizing PdO and CuO particles against agglomeration at high temperature treatment. This confirms our above assumptions from XRD analysis.

3.4. H_2-TPR

Figure 5 shows the TPR profiles of $Ce_{0.7}Zr_{0.3}Ba_{0.1}O_{2.1}$ and PdO/CZB catalysts with various PdO contents. The H_2-TPR profile of CZB is characterized by two peaks (α and β) at around 380 and 560°C, which are ascribed to the reduction of two different oxygens of CeO_2 [17]. However, barium oxide shows no reduction peak at temperatures below 900°C. The TPR profile of PdO shows a single peak at about 220°C, which is characterized by a γ peak (Figs. 5b–5d), which indicates that the highly dispersed palladium species exist on the surface of CZB. However, from Figs. 5b–5d, the intensity and the area of the γ peak are greatly increased with increasing the content of PdO. In addition, it can also be found that the supported palladium oxide dramatically changes the reduction behavior of CZB. In the case of the PdO/CZB catalysts, the intensity and area of α and β peaks were significantly changed after PdO supported on CZB. We found that this phenomenon can be explained by the synergistic interaction between PdO with CZB, promoting the oxygen transfer from the PdO to the support surface during the reaction process. This corresponds well to the results reported by Serre [18], Dow [19], and Jin [20], in which they indicated that the interfacial metal-support interaction strongly affects the CO oxidation activity.

3.5. XPS Analysis

In addition to the H_2-TPR analysis, the surface oxygen was further investigated by using XPS analysis. However, for the 0.25 wt % PdO/CZB catalyst, the O1*s* profile was generally decomposed into three components by fitting the data using a Gaussian/Lorenzian lineshape (Fig. 6). Two types of oxygen species can be clearly observed in the 0.25 wt % PdO/CZB catalyst. The main peak can be roughly divided into two peaks: a big one at 527.9 eV with a shoulder peak at 529.5 eV, and then a small peak at 534.1 eV. According to the literature, we attribute the O1*s* peaks at about 527.9 eV, and 529.5 eV to the metal oxide of PdO, while the small peak at 534.1 eV is mainly attributed to the adsorbed oxygen on the catalyst surface [21]. Table 2 presents the values of the binding energies for $Pd3d_{5/2}$ on the PdO/CZB catalyst with different PdO loading catalysts. The particle sizes of PdO in each catalyst determined by TEM are also listed. In Table 2, we note that the $Pd3d_{5/2}$ of these catalysts showed a slight decrease in the binding energies with the increase of PdO loading. Simultaneously, the chemistry shift of the $Pd3d_{5/2}$ is found to increase compared with pure PdO reported in the literature [22]. This indicates that the change of $Pd3d_{5/2}$ herein is responsible for the strong metal–support interaction between PdO and CZB. On the basis of the results indicated above, we think it is clear the fine interaction of active sites with support of CZB plays an important role in CO catalytic oxidation. This is consistent with the report by Haruta et al. [23]. Moreover, small particles may have higher binding energies [24]; thus, the nanosized particles can easily supply active sites for CO oxidation and enhance the oxidation activity of CO.

Table 2. Binding energy of the $Pd3d_{5/2}$ peak for PdO/CZB

	Catalysts		
	1.0% PbO/CZB	0.75% PdO/CZB	0.25% PdO/CZB
$Pd3d_{5/2}$, eV	338.5	338.8	339.2
d, nm	49	52	56

4. CONCLUSIONS

The above results suggest that doping barium into ceria–zirconium mixed oxide and using it as a catalyst support is an efficient way. The advantages of CZB support can enhance the supported PdO and CuO catalysts in their catalytic activity and thermal stability. This may be a new development direction of nanosized materials. We proposed that the strong interaction between nanosized PdO and CuO with the CZB support is responsible for low-temperature CO oxidation.

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