



Article Noble Metal-Free Ceria-Zirconia Solid Solutions Templated by Tobacco Materials for Catalytic Oxidation of CO

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Abstract: A series of ceria-zirconia solid solutions were synthesized using tobacco leaves, stems and stem-silks as biotemplates. A combination of physicochemical techniques such as powder X-ray diffraction (XRD), N₂ adsorption/desorption measurement, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to characterize the as-synthesized samples. The results show that the morphologies of the templates were well replicated in the obtained ceria-zirconia solid solutions. Catalytic oxidation activities of CO over the ceria-zirconia solid solutions were then investigated. The catalyst templated by tobacco stem-silk exhibited higher conversion of CO at lower temperature than that of ceria-zirconia solid solutions templated by tobacco leaves and stems or without templates due to its special morphology. The catalyst even showed similar CO conversion when compared to ceria-zirconia solid solutions doped with 1.0 wt % noble metals such as Pt, Ag and Au. The results highlighted the advantages of using tobacco as biotemplate.

Keywords: ceria-zirconia solid solutions; catalytic oxidation; CO; tobacco biotemplates

1. Introduction

Catalytic oxidation of CO at low temperature is becoming increasingly important recently due to its significance in pollution control for automobile exhausts and many industrial processes [1,2]. Cerium oxide, which is an important and less expensive rare earth oxide, has been widely investigated for applications to reduce the emissions of CO, NO_x, and hydrocarbons from automobile exhausts [3–5]. However, pure ceria is not very usable because of its relatively low oxygen storage capacity (OSC) and poor thermal stability [6]. To enhance the redox properties and thermal stability of pure ceria, zirconia (ZrO₂) is often mixed as an additive to form solid solutions of the Ce_{1-x}Zr_xO₂ type ($x \le 0.5$). For example, a three way catalyst (TWC) allows simultaneous conversions of CO, HCs and NO_x to innocuous compounds. CeO₂-ZrO₂ mixed compound, which act as an oxygen storage component to maintain the air to fuel ratio close to stoichiometric is present in the washcoat deposited on either a ceramic or metallic monolith [7,8]. A number of methods have been developed for the syntheses of Ce_{1-x}Zr_xO₂ solid solution including solid-state synthesis [9], high-energy milling [10], hydro/solvothermal synthesis [11,12], co-precipitation [13,14], the citrate method [15], inverse

micelles [16], and template method [17]. $Ce_{1-x}Zr_xO_2$ solid solutions prepared by different methods showed different activities for CO oxidation [18,19]. It seems that T_{50} , light-off temperature, the reaction temperature at 50% CO conversion, by using ceria-zirconia solid solution without any doping is usually high, and it continues to be a challenge to develop ceria-zirconia solid solution catalyst with lower T_{50} .

The OSC, reducibility, and catalytic activity of $Ce_{1-x}Zr_xO_2$ solutions often depend closely on their microstructures, including crystal size, orientation and morphology [20,21]. The use of templates is an attractive alternative to solve the above-mentioned case concerning the fabrication control and its influence on the interfacial properties. For example, mesoporous phases of ceria- zirconia solid solutions were synthesized using KIT-6 and SBA-15 silica as hard templates [22]. Recently, biotemplating methods have attracted much attention for the preparation of porous inorganic materials, because the approaches to obtain morphology-controllable materials with structural specificity and related unique functions. Furthermore, biological templates are often green and can be harvested in large amounts at low costs so that the method is environment benign and has little requirement for instrumentation [23–25]. However, the application of these biotemplated materials in selective oxidation was still very limited. For example, MFI-type zeolite frameworks with hierarchical porosity and complex architecture templated by Luffa sponge showed catalytic activity for cracking of *n*-hexane with no need for ion-exchange [26]. In our group, rice husks [27], natural rubber latex [28], and reed leaves [29] were used as templates in the preparing of cobalt doped porous titania-silica, mesoporous alumina, and mesoporous silica, which exhibited good catalytic activity for the selective oxidation of 4-methyl pyridine, tetralin, and limonene, respectively. They even offered significantly higher activity than same catalysts prepared by conventional templates such as poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide) (P123) [28]. However, biotemplate methods have not been used to prepare ceria-zirconia solid solutions so far as we know.

Herein, in the continuation of our work, tobacco leaves, stems and stem-silk were used as templates to synthesize a series of ceria-zirconia solid solutions. They displayed good catalytic properties for CO oxidation at lower temperature. This work will probably provide a new strategy for the utilization of bio-template in synthesis of ceria-zirconia solid solution.

2. Results and Discussion

2.1. Characterizations

The XRD patterns of the samples prepared with different Ce/(Ce + Zr) molar ratio are shown in Figure 1. All samples exhibit XRD patterns similar to cubic CeO₂ (JCPDS card 34-0394) and indicate the formation of stable solid solutions upon the introduction of Zr. Furthermore, all peaks gradually shifted to lower 2 θ values with the increase of Ce/(Ce + Zr) molar ratios. This phenomenon suggested that the interplanar spacing and cell parameters became bigger because of the isomorphous substitution of smaller Zr⁴⁺ (ionic radius 0.84 Å) with larger Ce⁴⁺ (ionic radius 0.97 Å) [30].

Nitrogen adsorption/desorption isotherms for the prepared ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios are shown in Figures S1–S4, respectively. The isotherms can be classified as being of type IV with H4 type hysteresis loop, which are characteristic of mesoporous material [31]. Table 1 shows a summary of BET (Brunauer-Emmett-Teller) specific surface area for the prepared ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios. It is seen that the surface area of synthesized ceria-zirconia solid solutions are higher than that of pure ceria or pure zirconia. In particular, ceria-zirconia solid solution without any template, CZ40 has highest BET specific surface area (112.08 m²/g). Interestingly, the biotemplating synthesis process seems not to have changed the BET surface areas of the ceria-zirconia solid solutions to the remarkable extent.



Figure 1. X-ray diffraction (XRD) patterns of the ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios (a) using no template; and using: (b) tobacco leaves; (c) tobacco stems; and (d) stem-silk as templates.

Table 1. Summary of BET (Brunauer-Emmett-Teller) specific surface area for the prepared ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios.

Samples	$S_{ m BET}$ (m ² ·g ⁻¹)	Samples	$S_{\rm BET}~({ m m}^2{ m \cdot}{ m g}^{-1})$	Samples	$S_{\rm BET}~({ m m}^2{ m \cdot}{ m g}^{-1})$	Samples	$S_{\rm BET}~({ m m}^2{ m \cdot}{ m g}^{-1})$
CeO ₂	58.78	leaves/CeO ₂	41.37	stems/CeO2	22.95	stem-silk/CeO2	48.35
CZ80	76.55	leaves/CZ80	95.61	stems/CZ75	55.93	stem-silk/CZ75	77.89
CZ60	91.80	leaves/CZ60	70.88	stems/CZ50	66.15	stem-silk/CZ50	99.47
CZ40	112.08	leaves/CZ40	66.24	stems/CZ25	42.73	stem-silk/CZ25	75.71
CZ20	96.31	leaves/CZ20	60.84	stems/ZrO ₂	39.56	stem-silk/ZrO ₂	22.49
ZrO_2	55.03	$leaves/ZrO_2$	42.02	-	-	-	-

Morphologies and microstructures of these ceria-zirconia solid solutions with 50% Ce/(Ce + Zr) molar ratios using tobacco materials as templates were studied by SEM and TEM. The biotemplates have a significant influence on the morphologies of the synthesized ceria-zirconia solid solutions. Figure 2a shows the SEM image of the tobacco leave templated ceria-zirconia solid solution. It is obvious that the microstructure of leaves/CZ50 is similar to the original leaves structure (Figure S5a).

Besides, some delicate leaf-like structures, such as stoma could be observed in leaves/CZ50 as shown in the magnified SEM image (Figure 2b). This implied that ceria-zirconia solid solutions using tobacco leaves as templates replicated the original morphology of the tobacco leaves. The microstructure of leaves/CZ50 is also characterized by TEM as illustrated in Figure 2c,d, revealing its sheet structure is composed of fine particles with sizes smaller than 10 nm. Figure 3a,b is the SEM images of stems/CZ50. It is obvious that the stems/CZ50 maintain the tubular structure of tobacco stems (Figure S5b). The stems/CZ50 is composed of fine particles with sizes smaller than 5 nm according to Figure 3c,d. The SEM images of stem-silk/CZ50 show the tubular structure of tobacco stem-silk-templated ceria-zirconia solid solutions as in Figure 4a,b. The well-aligned porous framework

is observed in µm scale. Stem-silk/CZ50 really retains the porous configuration of stem-silk faithfully (Figure S5c). The tubular morphology is also characterized by TEM as illustrated in Figure 4c. High magnification TEM image of stem-silk/CZ50 is shown in Figure 4d. These results fully demonstrate that the characteristic morphology of the templates appears to be replicated in the ceria-zirconia solid solutions exactly.



Figure 2. SEM (scanning electron microscopy) (**a**,**b**); and TEM (transmission electron microscopy) (**c**,**d**) images of leaves/CZ50.



Figure 3. SEM (a,b); and TEM (c,d) images of stems/CZ50.



Figure 4. SEM (a,b); and TEM (c,d) images of stem-silk/CZ50.

2.2. Catalytic Activity

Figure 5 shows the catalytic performance for CO oxidation over various ceria-zirconia solid solutions catalysts. T_{50} and T_{90} of all the catalysts are summarized in Table S1 and Figure 6. Figure 5a shows the catalytic activity profiles of CO conversion for the ceria-zirconia solid solution samples without templates. CO started conversion above 200 °C for all catalysts and increased sharply with rising temperature in Figure 5a. T_{50} and T_{90} (the reaction temperatures at 90% CO conversion) were found to decrease with decrease in Ce/(Ce + Zr) molar ratios. T_{50} and T_{90} of pure CeO₂ are 260 and 300 °C, whereas of CZ20 are 300 and 370 °C, respectively. The catalytic activity profiles of CO conversion for the ceria-zirconia solid solution samples templated by tobacco leaves are shown in Figure 5b. The CO conversion started above 300 °C higher than of samples without template. Except leaves/CZ80 the CO oxidation activities decreased with the decrease of Ce/(Ce + Zr) molar ratio. T_{50} and T_{90} of leaves/CZ80 are 515 and 660 °C, whereas of CZ20 are 674 and 776 °C, respectively. Figure 5c shows the catalytic activity profiles of CO conversion for the ceria-zirconia solid solution samples templated by tobacco stems. Different from those without templates, templated by leaves and stem-silk, the Ce/(Ce + Zr) molar ratios in the stem templated samples had little effect on the CO oxidation activities. Figure 5d shows the catalytic activity profiles of CO conversion for the ceria-zirconia solid solution samples templated by stem-silk. The catalytic activity of stem-silk templated catalysts appears a different result compare with those discussed above. The Ce/(Ce + Zr) molar ratios were either too low or too high led to lower oxidation activity. For example, T_{50} and T_{90} of stem-silk/CZ25 are 300 and 345 °C respectively. The stem-silk/CZ50 sample exhibited surprisingly high catalytic activity for CO oxidation at much lower temperatures than all the other samples in this study with T_{50} of 153 °C and T_{90} of 197 °C. Interestingly, even after loading of 1 wt % noble metals (Pt, Ag and Au), the CO conversions were not significantly increased compared with stem-silk/CZ50. For example, Pt-stem-silk/CZ50 showed the best catalytic activity, but compared with stem-silk/CZ50, the activity was only slightly increased. It is likely due to the stem-silk/CZ50 itself with high enough activity, there is almost no effect for lower temperature activity, even though Pt was impregnated on these

supports. On the other hand, noble metal catalysts usually require temperatures above 100 °C for efficient CO oxidation [32]. Thus, stem-silk/CZ50 ceria-zirconia solid solutions show great promise in the CO oxidation at low temperature without noble metals. For comparison, T_{50} and T_{90} of all the catalysts are summarized in Figure 6 and Table S1. The following trend was observed in terms of performance: stem-silk/CZ series > CZ series > stems/CZ series > leaves/CZ series. It should be pointed out that the catalytic activity has no direct correlation with surface areas. No significant difference was observed from the results of parallel trials and the results were randomly presented here. Moreover, only catalytic oxidation of CO over the as-prepared ceria-zirconia solid solutions was investigated in this research, but future work will be considered with hydrocarbons, H₂O (steam), CO₂ and oxides of nitrogen containing in the feed to simulate a real combustion exhaust more closely.



Figure 5. CO conversion as a function of temperature over ceria-zirconia solid solutions (a) without templates; and using: (b) tobacco leaves; (c) tobacco stems; and (d) tobacco stem-silk as templates with different Ce/(Ce + Zr) molar ratios.



Figure 6. T_{50} of CO oxidation over ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios.

2.3. Oxygen Storage Capacity

Generally speaking, OSC is recognized to improve the catalytic activity [33]. Therefore, OSC was measured by determining the H_2 consumption. The H_2 -TPR (temperature programmed reduction) profiles of ceria-zirconia solid solutions with 50% Ce/(Ce + Zr) molar ratios are shown in Figure 7. For all samples, there are two broad reduction peaks, the low temperature peaks at 350–415 $^{\circ}$ C and the high temperature peaks at 570–630 $^{\circ}$ C, which can be ascribed to the reduction of Ce⁴⁺ (surface Ce^{4+} and bulk Ce^{4+}) [34]. Note that the templates had strong effect on the areas and positions of the reduction peaks of samples. Leaves/CZ50 has the largest peak area and CZ50 exhibits the lowest top temperature. On the basis of TPR profiles, the reducibility and corresponding values of OSC for the ceria-zirconia solid solutions ranked in the following sequence: leaves/CZ50 (1976 μmol/g) > stems/CZ50 (1173 μmol/g) > stem-silk/CZ50 (1089 μmol/g) > CZ50 (999 μmol/g). It is expected that the leaves/CZ50 has fast bulk oxygen mobility and the best reducibility. However, this is not the case: leaves/CZ50, owing to the best reducibility and highest OSC, showed lowest oxidative activity for CO. These results show that the catalytic activity of ceria-zirconia solid solution for CO oxidation is not ascribed to its surface oxygen reducibility and bulk oxygen mobility. The highest catalytic activity of stem-silk/CZ50 for CO oxidation may be due to its special morphology. Yu and co-workers pointed out that the different morphologies gave rise to various oxygen vacancies and Ce⁴⁺ reduction extents of CeO₂, thus directly influencing their catalytic performance for the addressed reaction [35]. These results clearly demonstrate the morphology effect of ceria-zirconia solid solutions, regularly tubular morphology are most active. The Ce^{4+}/Ce^{3+} redox cycle could be more easily generated on the nanorods due to lower surface reduction energy of ceria on the 110 plane in previous literature [36–38].



Figure 7. H_2 -TPR (temperature programmed reduction) profiles of ceria-zirconia solid solutions with 50% Ce/(Ce + Zr) molar ratio.

3. Materials and Methods

3.1. Synthesis

The ceria-zirconia solid solutions using tobacco materials as templates were synthesized as follows: tobacco materials including tobacco leaves, stems and stem-silk after roasted were sheared to sheets with 1–2 cm length. The 10 g templates were firstly treated with 5% HCl for 12 h. Then, the templates were dehydrated gradually by ethanol a via a gradual solvent exchange process. The ceria-zirconia solid solutions using tobacco leaves as templates was synthesized by following incipient impregnation method via the reaction of cerium nitrate hexahydrate Ce(NO₃)₃·6H₂O, zirconyl nitrate hexahydrate ZrO(NO₃)₂·6H₂O, and citric acid in aqueous solution. In a typical synthesis of ceria-zirconia solid solutions using tobacco leaves as templates, a 20 mL aqueous solution containing 0.8598 g (0.002 mol)

of Ce(NO₃)₃·6H₂O, 1.8313 g (0.008 mol) ZrO(NO₃)₂·6H₂O and 4.2028 g (0.02 mol) citric acid was added into a closed vessel with immersing the as-treated templates for 3 days. After that, the samples were filtered, dried at 90 °C for 24 h. Finally, the as-treated samples were calcined at 500 °C in the air for 6 h to remove biotemplates. After naturally cooling to room temperature, faint yellow products were obtained. The ceria-zirconia solid solutions samples using tobacco leaves, stems and stem-silk as templates were denoted as leaves/CZ*x*, stems/CZ*x* and stem-silk/CZ*x* (*x* represents Ce/(Ce + Zr) molar ratio (%)), respectively. A similar procedure was applied in the preparation of conventional ceria-zirconia solid solutions except that in the absence of tobacco materials template was denoted as CZ*x* (*x* represents Ce/(Ce + Zr) molar ratio (%)). The noble metal catalysts supported on ceria-zirconia solid solutions were prepared by the conventional impregnation method [39]. The powder of ceria-zirconia solid solutions were impregnated with chloroplatinic acid, silver nitrate and chloroauric acid solution, respectively in order to prepare Pt, Ag and Au doped ceria-zirconia solid solutions. The loading of noble metal (Pt, Ag and Au) was set at 1.0 wt %. The mixture was dried at 110 °C for one day and calcined at 500 °C for 3 h in air.

3.2. Characterizations

Powder X-ray diffraction (XRD) experiments were conducted on a TTR III spectrometer with Cu K α radiation (Rigaku, Tokyo, Japan). Scanning electron microscopy (SEM) images of the samples were taken on a FEI Quanta 200FEG microscope (FEI, Eindhoven, The Netherlands). The transmission electron microscopy (TEM) images were obtained using a JEM-2100 microscope (JEOL, Tokyo, Japan). Pore size distributions, BET surface areas and pore volumes were measured by N₂ adsorption/desorption measurements using a Tristar 3020 gas sorption analyzer (Micromeritics, Norcross, GA, USA). H₂-TPR experiments were performed with a ChemBET PULSAR TPR/TPD (Quantachrome, Boynton Beach, FL, USA) equipped with thermal conductivity detector (TCD) under 10 vol. % H₂ flow diluted with Ar gas. A 0.05-g catalyst was exposed to a flow of H₂/Ar mixture. The temperature was ramped from room temperature to 800 °C at a heating rate of 10 °C·min⁻¹. After TPR measurement, the values of OSC were quantified by measuring the H₂ consumption. The amounts of H₂ consumption in the TPR process were calibrated with CuO reduction as a standard.

3.3. Catalytic Performance

Catalytic activity for preferential CO oxidation was tested using a self-made fixed-bed flow reactor About 100 mg of catalyst powder (60–80 mesh) was packed in a quartz glass U-tube reactor with 8 mm of inner diameter. The feed gas for the oxidation was about 1 vol. % CO balanced with Ar at a rate of 40 mL/min. CO oxidation experiments were performed in the temperature range 25–500 °C. The catalysts were heated at the rate of 10 °C/min and kept for 5 min at each reaction temperature before analysis of the product. Measurements were performed under the same reaction conditions. The concentrations of CO in the effluent gas were analyzed on-line by a GC-9790 gas chromatograph (Fuli Instruments, Taizhou, Zhejiang, China) equipped with a thermal conductivity detector (TCD) using He as carrier gas. The conversion of CO was calculated from the change in CO concentration between the inlet and outlet gases.

4. Conclusions

A series of ceria-zirconia solid solutions were synthesized using tobacco materials including tobacco leaves, stems and stem-silk as templates. The morphologies of the templates were well replicated in the ceria-zirconia solid solutions exactly. The stem-silk/CZ series showed higher CO oxidation activities. The CO conversions were slightly increased after loading of 1 wt % noble metal (Pt, Ag and Au) when compared to stem-silk/CZ50. The leaves/CZ50, owing to the best reducibility and highest OSC, showed lowest oxidative activity for CO. The catalytic activity of ceria-zirconia solid solution for CO oxidation is not ascribed to its surface oxygen reducibility and bulk oxygen mobility. The highest catalytic activity of stem-silk /CZ50 for CO oxidation may be due to its special

morphology. This work will probably provide a new strategy for the utilization of bio-template and synthesis of ceria-zirconia solid solution.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/6/9/135/s1, Figure S1: Nitrogen adsorption-desorption isotherms of the ceria-zirconia solid solutions without templates with different Ce/(Ce + Zr) molar ratios; Figure S2: Nitrogen adsorption-desorption isotherms of the ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios using tobacco leaves as templates; Figure S3: Nitrogen adsorption-desorption isotherms of the ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios using tobacco stem as templates; Figure S4: Nitrogen adsorption-desorption isotherms of the ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios using tobacco stem as templates; Figure S4: Nitrogen adsorption-desorption isotherms of the ceria-zirconia solid solutions with different Ce/Zr ratios using tobacco stem-silk as templates; Figure S5: SEM (scanning electron microscopy) images of tobacco leaves (a), stems (b) and stem-silk (c); Table S1: Summary of T_{50} and T_{90} for the prepared ceria-zirconia solid solutions with different Ce/(Ce + Zr) molar ratios.

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