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Facilely fabricating mesoporous nanocrystalline Ce-Zr solid solutions supported CuO based catalysts with advanced low-temperature activity toward CO oxidation

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Abstract

A series of mesoporous nanocrystalline Ce-Zr solid solutions with different Ce/Zr ratios were successfully synthesized by evaporation-induced self-assembly strategy, which were employed as the catalytic supports of CuO based catalysts for CO oxidation. These supports and catalysts were systematically characterized by X-ray powder diffraction (XRD), N₂ physisorption, Transmission electron microscopy (TEM), energy-dispersed spectroscopy (EDS) mapping, X-ray photoelectron spectroscopy (XPS), H₂ temperature programmed reduction (H₂-TPR), CO₂ temperature programmed desorption (CO₂-TPD), etc. The catalytic performances toward CO oxidation had been carefully evaluated over these CuO based catalysts. The effects of various influencing factors, such as Ce/Zr ratio, mesostructure, redox property of the support, CuO loading amount

and calcination temperature, on the low-temperature catalytic activity had been warefull $\frac{1}{9}/CGCV01612K$ investigated. The results showed that the catalyst supported on the support with the Ce/Zr ratio of 80/20 performed the highest catalytic activity. It was also found that the Ce-Zr solid solution mesoporous catalysts exhibited much higher catalytic activity than the counterparts without evident mesostructure, demonstrating the advantages of mesoporous catalysts by providing more accessible catalytic active sites. Besides, the mesoporous Ce-Zr solid solution supported catalysts with excellent redox property displayed much better catalytic performances than the commercial γ -Al₂O₃ supported catalyst. The kinetic study also indicated that the apparent activation energy of the CO oxidation process was greatly affected by the Ce/Zr ratio, mesostructure, and redox property of the support. Overall, the present CuO based catalysts with mesoporous nanocrystalline Ce-Zr solid solutions as support were considered as a series of promising catalysts of CO oxidation.

Keywords: Mesoporous structure; Ce-Zr solid solution; CuO catalyst; CO oxidation; Low-temperature catalytic activity

1. Introduction

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With the rapid development of global economy, carbon monoxide (CO) emission has been increasing year by year, which is mainly derived from the industrial & automobile exhausts and other living activities. CO is commonly considered as a sort of flammable, explosive, and toxic atmospheric pollutant, which has been greatly harmful to the human health and living environment.^{1, 2} In order to abate the emission of CO, its catalytic oxidation is considered as the most efficient solution. Up to now, the catalyst systems for the CO catalytic oxidation are mainly referred to noble metals and transition metal oxides based supported catalysts. The noble metals (Pt, Au, etc.) based supported catalysts have attracted widespread research interests due to their excellent low-temperature catalytic activities.^{3, 4} For instance, the application of Au based catalyst in CO oxidation can achieve the complete conversion of CO to CO₂ at -70°C.⁵ As a comparison, the traditional metal oxides based catalysts usually require relatively higher temperatures to achieve excellent activity. However, the high cost and rare availability of the noble metals restrict their wide application. Therefore, the development of metal oxides (such as CuO, Co₃O₄, etc.) based supported catalysts with high catalytic activities has received more and more attention considering their economical properties.^{6, 7}

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Among the transition metal oxides, the Co₃O₄ have been widely investigated because of itts^{9/C9CV01612K} excellent low-temperature catalytic activity, which displayed excellent catalytic activities comparable to the noble metal based catalysts.^{8, 9} However, the Co₃O₄ based catalysts usually suffer from the rapid deactivation when working in the high humidity environment. As a comparison, CuO performs robust tolerance toward the moisture in spite of relatively poor low-temperature activity.¹⁰ Therefore, the fabrication of CuO based catalysts with excellent low-temperature activity has been the research spotlight and challenge in the field of CO oxidation.

In order to design and fabricate highly efficient CuO based catalysts, the influences of the catalytic support and fabrication strategy have been widely investigated. Up to date, various catalytic supports, such as Al₂O₃,^{11, 12} SiO₂,^{13, 14} CeO₂,¹⁵⁻¹⁷ TiO₂,¹⁸⁻²⁰ Ce_xZr_{1-x}O₂,²¹ etc, have been extensively investigated. Among varieties of proposed CuO based catalysts, the CuO-CeO₂ based metal oxides catalysts have attracted great interests in CO oxidation due to their excellent redox properties as well as low cost.²² Because their catalytic performances are usually comparable to or even superior to the precious metal based catalysts.²³ The reason might be that the Cu species is greatly active and exhibits excellent co-chemical adsorption by $Cu^{2+}-Cu^+$ couple. At the same time, CeO₂ support possesses the storage and release capacity of oxygen and promotes the dispersion of Cu active centers. Specifically, it is provided with oxidative coupling Ce⁴⁺/Ce³⁺ to activate more oxygen molecules during the process of CO oxidation.²⁴ Therefore, CuO-CeO₂ based catalysts have been widely used for catalyzing the CO oxidation.^{25, 26} However, the pure CeO₂ usually exhibits poor thermal stability. It was reported that the doped transition metal oxide (such as ZrO_2 , PrO_x , etc.) structural modification of the CeO₂ lattice can obviously improve the stability of CeO₂ when calcined at high temperature.²⁷ For instance, although ZrO₂ cannot directly participate in the catalytic reaction, the incorporation of zirconium into CeO₂ lattice can modify the structure or the site of CeO_2 crystallite by forming the Ce-Zr solid solution, which greatly improves the oxygen storage capacity (OSC), the redox property, thermal stability, and the dispersion of the obtained mixed oxides.^{28, 29} As a result, its catalytic performance in the oxidation processes, such as CO oxidation and CO₂ reforming of CH₄, can be greatly improved.^{30, 31} Chen et al.³² studied the effects of different Ce/Zr ratios for the CuO/Ce_xZr_{1-x}O₂ on the catalytic performances toward CO catalytic oxidation. Manzoli et al.³³ found that both CeO₂ and ZrO₂ can enhance the activity of copper and only the copper clusters in close proximity to the CeOppart OP/C9CYO1612KCe_xZr_{1-x}O₂ have higher specific activity at low reaction temperature toward CO oxidation. It was supposed that CuO supported on Ce-Zr solid solutions can enhance the oxidation activity of CO by synergistic effect between CuO and Ce-Zr solid solutions.³⁴

As well known, the supported catalysts with different morphologies and dispersion of CuO species can be prepared by deposition-precipitation, co-precipitation, impregnation and sol-gel, etc.³⁵⁻³⁷ Compared with traditional catalytic support, the mesoporous metal oxides commonly possess higher surface areas, bigger pore volumes, and more uniform pore channels. Therefore, they can be used as the efficient catalytic support or catalysts for oxidation of CO.^{38, 39} The researchers have devoted great efforts to the development and fabrication of mesoporous metal oxides, such as Co₃O₄,^{40, 41} TiO₂,^{42, 43} Al₂O₃,^{44, 45} CeO₂,^{46, 47} ZrO₂,⁴⁸ Ce_xZr_{1-x}O₂,³¹ etc, which have been investigated as the catalytic supports. If the mesoporous Ce-Zr solid solution was used as the catalyst surface after calcination were supposed to be obtained due to the abundant pores and large surface area, thus possessing the great potential to further improve the catalytic performance by providing sufficient accessible CuO active centers to the gaseous feed stocks.⁴⁹

Herein, a series of mesoporous nanocrystalline Ce-Zr solid solution with different Ce/Zr ratios were proposed and successfully synthesized by the evaporation induced self-assembly (EISA) strategy.³⁰ The obtained materials with outstanding textural properties and thermal stability were employed as the catalytic supports for CuO based catalysts. A series of CuO based catalysts supported on the mesoporous supporter were prepared via incipient wetness impregnation method for CO oxidation at low temperature. The supports and catalysts were systematically characterized by X-ray powder diffraction (XRD), N₂ physisorption, Transmission electron microscopy (TEM), energy-dispersed spectroscopy (EDS) mapping, X-ray photoelectron spectroscopy (XPS), H₂ temperature programmed reduction (H₂-TPR), CO₂ temperature programmed desorption (CO₂-TPD), etc. The effects of different Ce/Zr ratio, CuO loading amount, calcination temperature, mesostructure, and the redox property of the support on the low-temperature catalytic activities of catalysts for CO oxidation were systematically and carefully investigated.

2. Experimental

2.1The synthesis of the mesoporous nanocrystalline Ce-Zr solid solutions

Mesoporous nanocrystalline Ce-Zr solid solution with different Ce/Zr ratios were synthesized by evaporation induced self-assemble (EISA) strategy according to the protocol reported in previous literatures.^{30, 50} Specifically, 1.0 g of Pluronic P123 (M_{av} = 5800, EO₂₀PO₇₀EO₂₀, Aladdin) was first dissolved in 20 mL of ethanol with vigorous stirring. Then, quantitative Ce(NO₃)₃·6H₂O (Shanghai Macklin Bio-Chem Co., Ltd., China) and ZrOCl₂·8H₂O (Shanghai Aladdin Bio-Chem Co., Ltd., China) were added in sequence (the total amount of Ce and Zr was 10 mmol). After vigorous agitation at room temperature for at least 2 h, the transparent homogeneous sol was transferred to the Petri dish covered with a perforated PE film. The EISA process was carried out in the oven with desired temperature (60°C) and humidity (< 50%). After 48 h EISA process, the xerogels product was further dried at 100°C oven for at least 12 h and golden yellow or brown yellow xerogel was obtained. The colour of the xerogel deepened with the increase of the Ce content. Calcination was carried out by slowly increasing temperature from room temperature to 500°C with a ramping rate of 1°C/min and kept at 500°C for 5 h in air atmosphere. The finally obtained material was ground into the fine power. The mesoporous materials were labelled as M-CexZry-T, where "M" represented "mesoporous", "x" and "y" denoted the molar percentage content of Ce and Zr, respectively, and "T" referred to the calcination temperature of the material.

In order to investigate the effect of the mesoporous structure on the catalytic performance, the Ce-Zr solid solution without obvious mesostructure was denoted as N-CexZry-T, where N stood for non-mesoporous and the meanings of x, y, and T were the same as those of M-CexZry-T. The preparation method of N-CexZry-T and M-CexZry-T was greatly identical without the addition of P123 template.

2.2 Catalyst preparation

CuO based supported catalysts containing z wt% CuO (z wt% = $m_{CuO}/(m_{CuO} + m_{carrier}) \times 100\%$) were synthesized by employing incipient impregnation method with Cu(NO₃)₂·3H₂O (Sinopharm Chemical Reagent Co., Ltd., China) as the precursor of CuO. After impregnation, the catalyst precursors were dried in the 60°C oven for at least 12 h. Then, the calcination was conducted at 500°C for 5 h. The obtained catalysts with different CuO containing loading amounts were denoted as z%CuO/M-CexZry-T and z%CuO/N-CexZry-T in the following text. In order to

clarify the effect of the calcination temperature on the properties of the catalyst, a series 1019/C9CY01612K catalysts calcined at different temperature were prepared according to the identical procedure.

Besides, the CuO based catalyst supported on commercial γ -Al₂O₃ (C-Al₂O₃) support (abbreviated as *z*%CuO/C-Al₂O₃-T) was also investigated to reveal the role of redox property of the mesoporous Ce-Zr solid support in promoting the catalytic activity toward CO oxidation process.

2.3 Catalyst characterizations

X-ray powder diffraction (XRD) patterns were collected on a XRD-6100 diffractometer (Shimadzu, Japan) using Cu K α radiation at 40 kV and 100 mA in a scanning range of 20°–80° (2 θ) with a step length of 0.02° at a scanning rate of 3°/min.

 N_2 adsorption-desorption analyses were collected using an Autosorb-iQ-AG-MP instrument (Quantachrome, US) at -196°C. Before the measurement, samples were degassed at 300°C for at least 3 h. The specific surface areas of the catalysts were calculated by the multipoint Brunauer–Emmet–Teller (BET) method. The pore size distributions and pore volumes were calculated from the adsorption branches of the N_2 isotherms by using the Barett–Joyner–Halenda (BJH) method.

Transmission electron microscopy (TEM) images, scanning transmission electron microscopy (STEM) images, selected area electron diffraction (SAED), and energy-dispersed spectroscopy (EDS) mapping measurements were carried out on a high-resolution transmission electron microscopy (FEI TECNAI G2 F20) with accelerating voltage of 200 kV. For the samples preparation, they were firstly dispersed in absolute ethanol together with 30 min ultrasonic and then deposited on a carbon-coated copper grid.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an Escalab 250Xi (Thermo Fisher Scientific, US) spectrometer. The powder of the sample were spread and coated on the conductive tape on the sample holder. The binding energies were calibrated using the C 1s line at 284.5 eV as the reference.

 H_2 temperature programmed reduction (H_2 -TPR) experiments were performed on homemade fixed bed reactor and the consumption of H_2 was recorded by a LC-D200 mass spectrometer (TILON, US) by using 200 mg catalyst under the mixture of 5 vol% H_2 -95 vol% Ar stream (50 mL/min). Prior to the H_2 -TPR measurements, the samples were purged with the Ar stream at 300°C for 30 min and cooled down to room temperature. Then, 5 vol% H_2 -95 vol% Ar mixture

was introduced and the programmed temperature was conducted with a ramping heating@rate1@P/C9CY01612K 20°C/min to 800°C. The hydrogen consumption was measured using a LC-D200 mass spectrometer.

 CO_2 temperature programmed desorption (CO_2 -TPD) measurements were carried out on the same instrument as the H₂-TPR. Typically, the 100 mg of catalyst was exposed under pure CO_2 stream (20 mL/min) for 30 min at 25°C to accomplish the chemisorption of CO_2 . Then, the sample was purged with Ar stream at 25°C until the baseline of CO_2 in the mass spectrum was stable. Finally, the CO_2 -TPD was carried out with a ramping heating rate of 20°C/min from the 25°C to the 800°C under Ar stream (40 mL/min).

2.4 Catalytic activity measurements

Catalytic activity tests for CO oxidation were carried out in a vertical fixed-bed continuous flow quartz reactor. The entire reaction and analysis system consists of three parts: (1) the mass flow controlling unit (Brooks Instruments), (2) the reactor unit (homemade furnace), and (3) the analysis unit (PerkinElmer Gas Chromatography Clarus 680). Typically, the 100 mg of catalyst was placed over the quartz wool in the quartz tube of the fixed-bed reactor. The feed gas consisting of 1 vol% CO, 20 vol% O₂ and balanced N₂ with a total flow rate of 20 mL/min, corresponding to the gas hourly space velocity (GHSV) of 12000 mL/(g·h) gas, was introduced into the reactor and investigated with designated temperature range. Finally, the effluent gas were analyzed on line using the GC-680 Perkin Elmer gas chromatography equipped with a thermal conductivity detector (TCD). The catalytic activity was reflected and expressed in the form of CO conversion. Therefore, the CO conversion (abbreviated as Cco) can be calculated based on the carbon balance according to the following formula, where the $F_{CO, inlet}$ and $F_{CO, outlet}$ represented the flow rate of CO species into and out of the reactor.

$$C_{\rm CO} = (F_{\rm CO, inlet} - F_{\rm CO, outlet}) / F_{\rm CO, inlet} \times 100\%$$
(1)

3. Results and discussion

3.1 Characterization of support

3.1.1 X-ray diffraction analysis

Fig. 1 (1) showed the XRD patterns of mesoporous Ce-Zr solid solutions with different Ce/Zr ratios calcined at 500°C. As well known, the Ce-Zr solid solutions could usually exist in the form of three stable phases (monoclinic (m), tetragonal (t), cubic (c)) and two metastable phases (t', t")

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under different fabrication and calcination conditions.⁵¹ It could be observed that almost all these/CSCYO161280 mesoporous Ce-Zr solid solution samples displayed wide and well-defined XRD peaks, indicating that all the samples were in crystalline state. Besides, it was also worth noting that these samples exhibited four pronounced diffraction peaks around $2\theta = 28.6^{\circ}$, 33.04° , 47.4° and 56.36° , suggesting the presence of the cubic crystalline structure similar to the cubic CeO₂ (PDF#34-0394). It was also of great interest to find that the diffraction peaks of these materials gradually shifted to the lower angle direction with the increase of the Ce content from 0% to 100%. The reason for this was that the ionic radius of Ce⁴⁺ (0.101 nm) was a bit larger than that of Zr⁴⁺ (0.086 nm). Specifically, when the Zr⁴⁺ in ZrO₂ was partly replaced by the Ce⁴⁺, the unit cell of Ce-Zr solid solution (Ce_xZr_{1-x}O₂) would become large, thus causing the shift of the XRD peaks to the lower 2 θ angle region. There was no ZrO₂ or CeO₂ individual diffraction peak observed over these mesoporous Ce_xZr_{1-x}O₂ solid solution samples. This suggested that the phase separation between ZrO₂ and CeO₂ did not take place and homogenous Ce-Zr solid solution could be finally formed.^{52,53}

The XRD patterns of Ce-Zr solid solution (N-Ce50Zr50-500) prepared without P123 template and commercial Al₂O₃ were shown in Fig.1 (2). It was noticeable in the figure that the N-Ce50Zr50-500 displayed characteristic diffraction peaks of the Ce-Zr solid solution, demonstrating that the form of Ce-Zr solid solution crystalline phase was not greatly affected by the P123 template. As for the commercial alumina support, it displayed the featured diffraction peaks of γ -Al₂O₃ (PDF#04-0880).

3.1.2 N₂ physisorption analysis

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In order to investigate the structural properties of these catalyst supports, N₂ physisorption analysis was conducted. The N₂ adsorption–desorption isotherms (panel A) and the corresponding pore size distribution curves (panel B) were shown in Fig. 2, respectively. It could be observed in Fig. 2A (1) that almost all the M-CexZry supports exhibited IV type isotherms with H2-shaped hysteresis loops, which were the typical feature of the mesoporous channels with ink-bottle shape. In addition, their pore size distribution curves in Fig. 2B (1) displayed narrow pore size distribution curves centered around 4.3-7.9 nm. This further confirmed that the pore diameters of these catalytic supports were located in the range of mesopore (2.0-50.0 nm). Besides, the structural properties of N-Ce50Zr50-500 and C-Al₂O₃ reference supports were also carefully

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investigated. As shown in Fig. 2A (2), the isotherm of N-Ce50Zr50-500 preparing without P1239/C9CY01612K templating agent is of type IV with H3 shaped hysteresis loop, which was great different with the corresponding M-Ce50Zr50-500 counterpart. The H3 hysteresis loop showed an irregular mesopore structure with wedge shape, indicating that P123 templating agent played a crucial role during the process of constructing mesoporous structure with specific shapes. At the same time, the pore size distribution of N-Ce50Zr50-500 in Fig. 2B (2) was very wide without obvious pore size distribution peak. Therefore, it was supposed that the mesoporous structure of N-Ce50Zr50-500 might be derived from the disordered stacking of the Ce-Zr solid solution nanoparticles rather than the assembly around the P123 templating agent. As for the C-Al₂O₃ commercial support, it presented the IV type isotherms with H2 shaped hysteresis loop and relatively narrow pore size distribution around 4.3 nm. This suggested the presence of mesostructure among the C-Al₂O₃ support.

The specific structural properties of the above discussed materials were summarized in Table 1. It was worth noting that the as-prepared mesoporous Ce-Zr solid solutions exhibited large BET specific surface areas of up to 72.7 m²/g, big pore volumes of up to 0.12 cm³/g, and average pore diameters in the range of mesoporous size (4.3-7.9 nm). Compared with N-Ce50Zr50-500, M-Ce50Zr50-500 performed much larger BET specific surface area and bigger pore volume, once more demonstrating a significant effect of the P123 templating agent on the structural properties of the materials.

3.1.3 TEM, SAED, STEM, and EDS-mapping analyses

The TEM and SAED analyses of mesoporous Ce-Zr solid solution images were carried out and shown in Fig. 3. The M-Ce50Zr50-500, M-Ce60Zr40-500, and M-Ce80Zr20-500 had been selected as the presentative samples with different Ce/Zr ratios. The mesoporous structure with a worm-like porous network formed by the stacking of Ce-Zr solid solution nanoparticles could be directly observed in Fig. 3 (a, b, d, e, g, h). It was assumed that the Ce-Zr precursors assembled along the P123 template during the process of EISA and small nanoparticles could form after the calcination process. Besides, the crystalline structural details of the nanoparticles were further investigated by high resolution transmission electron microscopy (HRTEM) and their images as shown in Fig.3 (c, f, i). The lattice fringe spacing of the investigated samples with different Ce/Zr ratios was in the range of 0.299-0.309 nm, which could be attributed to the (1 1 1) crystal plane of we we well consistent with those of the XRD analysis in Fig. 1 (1).

The spatial dispersion of Ce and Zr elements among the mesoporous structure could be determined by the scanning transmission electron microscopy (STEM) together with the energy dispersive spectrometer mapping (EDS-mapping) of the mesoporous Ce-Zr solid solution samples. M-Ce50Zr50-500, M-Ce60Zr40-500, and M-Ce80Zr20-500 are selected as the representatives and their STEM images and EDS-mapping element diagrams were shown in Fig. 4. It can be seen that the distribution of Ce and Zr in the catalyst carrier was uniform over these three investigated samples. This indicated that the phase separation between CeO₂ and ZrO₂ did not take place and uniform solid solution could be achieved by one-pot EISA strategy, which was also confirmed by the XRD analysis in Fig. 1 (1).

3.1.4 H₂-TPR analysis

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Fig. 5 showed the H₂-TPR profiles of M-CexZry-500 catalyst supports. Only one pronounced reduction peak could be observable over these samples with different Ce/Zr ratios in the range of 620-750 °C, which might be derived from the reduction of Ce⁴⁺ on the surface. Generally, it was reported that Ce⁴⁺ or pure cerium dioxide could be reduced to Ce³⁺ at 780°C or even higher temperature, which was a bit higher than the reduction peaks in this figure.²⁵ Therefore, the Ce⁴⁺ could be reduced to Ce³⁺ at relatively lower temperature in the form of mesoporous Ce-Zr solid solution. In addition, the position of reduction peak was closely related to the ratio of Ce/Zr.^{52, 54} Specifically, with the incorporation of Zr species, the reduction peak could move to the lower temperature region around 650°C. This phenomenon implied that the introduction of Zr⁴⁺ cation into the CeO₂ crystalline matrix could enhance the reducibility of the Ce⁴⁺ species.

3.2 Catalyst characterization

3.2.1 XRD analysis

Fig. 6 (1) showed the XRD patterns of 20CuO/M-CexZry-500 catalysts with identical CuO loading amount supported on the carriers with different Ce/Zr ratios calcined at 500°C. It was of great interest to find that the intensities of the CuO diffraction peaks (PDF#45-0937) were greatly similar due to the identical CuO loading (20 wt%) over most of the catalysts. As for a bit stronger

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CuO peak intensity over 20CuO/M-Zr100-500 than other catalysts, it could be attributed to the COCYO1612Kpoor dispersion of CuO species over M-Zr100-500 support owing to its low specific surface area and small pore volume. It was also worth noting that the diffraction peak of Ce-Zr solid solution still migrated to a lower 20 value with the increase of Ce/Zr ratio due to the difference of Ce⁴⁺ and Zr⁴⁺ in cation radius. As a comparison, the diffraction peak of CuO did not suffer any change in the 20 value.

The XRD patterns of z%CuO/M-Ce80Zr20-500 catalysts with different CuO loading amounts were displayed in Fig. 6 (2). It was of great interest to find that the intensity of CuO diffraction peaks gradually increased with the increase of the CuO content from 0 wt% to 30 wt%. This suggested that the dispersion of CuO species over the catalyst surface gradually decreased with the increase of the loading amounts. Therefore, the growth of the crystalline size of the CuO nanoparticles would take place.

Fig. 6 (3) performed the XRD patterns of 15CuO/M-Ce80Zr20-T catalysts calcined at different temperatures. For the catalysts calcined below 600°C, they displayed $Ce_{0.8}Zr_{0.2}O_2$ and CuO diffraction peaks in similar intensities. This indicated that the CuO species were successfully confined within the mesopore. As a result, both the severe thermal sintering of the CuO nanoparticles and collapse of the mesoporous framework were successfully avoided when the calcination temperature was below 600°C. As for the 15CuO/M-Ce80Zr20-700 sample, it displayed much stronger CuO and $Ce_{0.8}Zr_{0.2}O_2$ diffraction peaks than other samples calcined at lower temperatures. This ought to be attributed to the collapse of the mesoporous framework as the calcination temperature as high as 700°C, which made the dispersion of CuO become worse.

In order to investigate the CuO dispersion over different catalytic supports, the 20CuO/N-Ce50Zr50-500 and 15CuO/C-Al₂O₃-600 also carefully analyzed and their XRD patterns were exhibited in Fig. 6 (4). The ratio of the intensity of CuO diffraction peaks of 20CuO/N-Ce50Zr50-500 and 20CuO/M-Ce50Zr50-500 were calculated to be 1.06 and 1.03 respectively, indicating that the dispersion of CuO on the mesoporous support was better owing to its good textural properties, such as large specific surface area, big pore volume, etc. As for the 15CuO/C-Al₂O₃-600, it also displayed a bit higher CuO diffraction peak intensity than 15CuO/M-Ce80Zr20-600, though C-Al₂O₃ support possessed much higher specific surface area

and pore volume than M-Ce80Zr20-600 support. This indicated that the CuO species had much /C9CY01612K stronger tendency to disperse over the surface of mesoporous Ce-Zr solid solution.

3.2.2 N₂ physisorption analysis

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Fig. 7 showed the N₂ adsorption-desorption isotherms (panel A) and pore size distributions (panel B) of the investigated catalysts in this study. As shown in Fig. 7A (1), (2) and (3), almost all of the 20CuO/M-CexZry-500, z%CuO/M-Ce80Zr20-500, and 20CuO/M-Ce80Zr20-T catalysts exhibited type IV isotherms with H2 shaped hysteresis loops, which were similar to their corresponding catalytic supports exhibited in Fig. 2A (1). Thus, the mesostructure of the M-CexZry-500 supports were successfully retained after the loading of CuO and the calcination of the catalyst precursors, once again demonstrating the excellent thermal stability of these catalytic supports. The corresponding pore size distribution curves of these mesoporous catalysts were shown in Fig. 7B (1), (2) and (3). The average pore diameter size of the catalysts were similar or even a bit larger than their corresponding carriers, indicating that the thermal shrinkage and collapse of the mesoporous skeletons had been effectively avoided during the process of catalyst fabrication and calcination. Besides, the structural properties of 20CuO/N-Ce50Zr50-500 and 15CuO/C-Al₂O₃-600 catalysts were also investigated. As can be observed in Fig. 7A (4) and Fig. 7B (4), both of these two catalysts displayed isotherms and pore size distributions similar to their respective supports in Fig. 2A (2) and Fig. 2B (2).

The results of structural properties of the as-prepared catalysts were summarized in Table 2. It was worth noting that the as-prepared mesoporous Ce-Zr solid solution catalysts still retained the large BET specific surface areas up to 56.3 m²/g, big pore volume ups to 0.14 cm³/g, and average pore diameters in the mesopore size. Generally, the catalysts displayed relatively lower specific surface areas and pore volumes than their corresponding supports. The reason for this ought to be attributed to the partly clogging of the mesoporous channels by the supported CuO species. In contrast, the average pore size exhibited similar or even greater values, displaying the outstanding thermal stability of the mesoporous framework of the Ce-Zr solid solution catalytic supports.

3.2.3 TEM and SAED analyses

The 10CuO/M-Ce80Zr20-500, 15CuO/M-Ce80Zr20-600 and 25CuO/M-Ce80Zr20-500 were selected as the representatives of mesoporous catalysts with different CuO loading amounts and

calcination temperatures for TEM and SAED analyses. Their images were displayed in Fig: 81439/C9CY01612K shown in Fig. 8 (a, c, e), the catalysts performed identical mesoporous structures to their supports in Fig. 3 and no obvious large CuO cluster could be obviously observed. This indicated that the CuO species were well dispersed among the surface of the mesoporous supports. In order to investigate the fine structural details of the nanoparticles, the HRTEM analysis had been also conducted and their images were shown in Fig. 8 (b, d, f). Compared with the mesoporous Ce-Zr solid solution carriers, the catalysts exposed new crystal faces with different lattice fringe spacings around 0.230 nm and 0.250 nm, which were attributed to the (1 1 1) and (0 0 2) crystal faces of CuO, respectively. As for the insets of Fig. 8 (a, c, e), the nanocrystals with clear diffraction rings were observed, showing the high crystallinity of these CuO based catalysts supported on mesoporous Ce-Zr solution. Besides, the TEM images of the 20CuO/N-Ce50Zr50-500 and 15CuO/C-Al₂O₃-600 reference catalysts were shown in Fig. 9. The CuO nano-cluster could be observed over the 20CuO/N-Ce50Zr50-500 sample. However, the worm-like mesopore channel was absent. This could be attributed to the poor CuO dispersion over N-Ce50Zr50-500 with low specific surface area and small pore volume. For 15CuO/C-Al₂O₃-600 catalyst, no special morphology was observed. However, the $(1\ 1\ 1)$ and $(0\ 0\ 2)$ crystal faces of CuO phase could be clearly observed over both reference catalysts in HRTEM images (Fig. 9 (c, f)), which was consistent with the results of the XRD analysis in Fig. 6 (4).

3.2.4 H₂-TPR analysis

In order to investigate the interaction between CuO and the supports, the H₂-TPR analyses of the as-prepared catalysts with different Ce/Zr ratios, CuO loading amounts, calcination temperatures, and catalytic supports were systematically carried out. Their H₂-TPR profiles were shown in Fig. 10.

The Fig. 10 (1) displayed the H₂-TPR profiles of 20CuO/M-CexZry-500 catalysts with different Ce/Zr ratios were displayed in Fig. 10 (1). As shown, almost all the catalysts exhibited similar hydrogen consumption profiles in the shape with a large reduction peak in the range of 432-510°C and a relatively small shoulder peak in the range of 197-237°C. For the CuO species in the free state, it usually had a reduction peak near 380°C.55 However, it was reported that the reduction temperature of CuO species was lower than the free CuO when supported on fluorite type oxides.^{56, 57} In this work, the XRD analyses in Fig. 1 (1) revealed that M-CexZry-500

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supports were in the form of fluorite structure. Therefore, the reduction peak around 210°C could/C9CY01612K be ascribed to the reduction of the CuO species, which had closely synergistic effect with the M-CexZry-500 supports. As a result, the CuO species could be reduced at relatively lower temperature. The M-CexZry-500 support could greatly promote the reduction of CuO to some degree.^{17, 58} However, the wide reduction peaks with strong intensity in the high temperature region (432-510°C) became a bit complicated. The main reason was the reduction of CuO species strongly interacted with the supports. They might also be attributed to the reduction of surface Ce⁴⁺ in the mesoporous Ce-Zr solid solution supports, which could also be partly reduced based on the H₂-TPR profiles in Fig. 5. However, compared with the H₂-TPR profiles of the M-CexZry-500 supports in Fig. 5, it could be found that the surface Ce^{4+} of the 20CuO/M-CexZry-500 catalysts could be reduced at relatively lower temperature. This could be ascribed to the synergistic effect between CuO and the M-CexZry-500 supports, which could also positively promote the reduction of Ce^{4+} species. For instance, the reduction temperature over M-Ce80Zr20-500 support was 620°C, which was much higher than the temperature of the second reduction peak (442°C) over 20CuO/M-Ce80Zr20-500 catalyst. Therefore, the presence of CuO was evidently beneficial to the reduction of surface Ce⁴⁺ species because of their synergistic effect.

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Fig. 10 (2) and (3) exhibited the H₂-TPR profiles of z%CuO/M-Ce80Zr20-500 catalysts with different CuO loading amounts and 15CuO/M-Ce80Zr20-T catalysts with different calcination temperatures, respectively. Similar to the H₂-TPR profiles of the 20CuO/M-CexZry-500 catalysts in Fig. 10 (1), two distinct reduction peaks could be observed, which could be attributed to the reduction of the CuO species with different interactions toward supports as well as the Ce⁴⁺ species in M-Ce80Zr20-500 support based on the above discussion. As for the H₂-TPR profiles of z%CuO/M-Ce80Zr20-500 catalysts in Fig. 10 (2), it could be noticeable that the H₂ consumption peak intensity gradually increased with the increase of the CuO loading from 10 wt% to 30 wt%. For the H₂-TPR profiles of 15CuO/M-Ce80Zr20-T catalysts calcined at different temperatures in Fig. 10 (3), it was of great interest to find that the positions of the reduction peaks gradually shifted toward the higher temperature, suggesting that the interaction between CuO and the M-Ce80Zr20 support became stronger with the increase of the calcination temperature.

Finally, the H₂-TPR curves of 15CuO/C-Al₂O₃-600 and 20CuO/N-Ce50Zr50-500: were/C9CY01612K shown in Fig. 10 (4). As shown in the figure, both catalysts performed two distinct reduction peaks around 275°C and above 450°C, which could be ascribed to the different CuO species with different interactions between CuO and support. In general, the characterization results of H₂-TPR were consistent with the characterization results of XRD.

3.2.5 XPS analysis

The surface composition of the catalysts was analyzed by the X-ray photoelectron spectroscopy (XPS) and the detailed information related to the chemical states of the metal cations and oxygen anions was obtained. The XPS profiles of Cu 2p, Ce 3d, Zr 3d, and O 1s of the 20CuO/M-CexZy-500 catalysts with different Ce/Zr ratios were exhibited in Fig. 11.

In Fig.11 (1), the XPS peaks centered at 954.0 eV and 934.0 eV could be corresponded to Cu $2p_{1/2}$ and Cu $2p_{3/2}$, respectively. Avgouropoulos and Ioannides reported that the presence of shake-up peaks in the range of 939.0-944.0 eV and a higher Cu $2p_{3/2}$ binding energy in the range of 933.0 eV-934.0 eV were two major XPS characteristics of CuO.¹⁵ In current spectra of the catalysts, the presence of Cu $2p_{3/2}$ peak around 934.0 eV, the shake-up peak in the range of 939.0-944.0 eV, and the W shaped peak belonging to Cu²⁺ satellite peak around 962.5 eV indicated the presence of CuO species over the surface of the 20CuO/M-CexZry-500 catalysts.

For the 20CuO/M-Ce80Zr20-500 catalysts, their spectra of Ce 3d could be split into eight peaks centered around 882.0 eV, 885.0 eV, 889.0 eV, 899.0 eV, 901.0 eV, 904.0 eV, 908.0 eV, 917.0 eV as shown in Fig. 11 (2). As can be seen in the figure, these peaks were similar in the shape and their intensities gradually enhanced as the Ce/Zr ratio increased. The peaks referred to V and U could be attributed to Ce 3d_{5/2} and Ce 3d_{3/2}, respectively. The peaks referred to U''' and V''' could be attributed to Ce⁴⁺. The U, V, U'' and V'' were shakedown features produced by one or two electrons moving from a filled O 2p orbit to an empty Ce 4f orbit. The presence of U' and V' were due to the existence of Ce³⁺ species.^{54, 59, 60} The Ce cations in most of the catalysts was mainly present in the form of Ce⁴⁺ but it had also been found the presence of Ce³⁺. In the case of the 20Cu/M-CexZry-500 catalysts, the U' and V' shoulder peaks could be observed, suggesting the presence of Ce³⁺ species. This would facilitate the activation of oxygen and redox recycling of the catalysts.

Fig. 11 (3) showed the Zr 3d XPS spectrogram of these catalysts. It can be clearly seen in the/C9CY01612K figure that the electron binding energy of Zr $3d_{5/2}$ was around 184.5 eV. This was the typical feature for the presence of Zr⁴⁺ on the surface of these mesoporous catalysts. Besides, the peak intensity of Zr 3d gradually decreased with the increase of the Ce/Zr ratio, which could be ascribed to the decrease of the surface Zr⁴⁺ concentration.^{61, 62}

As for the O 1s, it can be seen from Fig.11 (4) that its profile was provided with a main peak near 530.0 eV and a shoulder peak near 533.0 eV. Based on previous literatures, the shoulder peak near 533.0 eV should be corresponding to the O²⁻ species associated with the Ce³⁺, usually generating oxygen pockets or vacancies around it in order to maintain the neutrality of the charge.^{54, 63} Therefore, the shoulder peak of the O 1s at high binding energy was finally formed. Besides, the O 1s peak of the catalysts were further investigated in detail by employing the peak fitting method and the results related to the areas of O 1s peaks were shown in Table 3. It could be seen in the table that the mesoporous Ce-Zr solid catalysts exhibited a bit bigger ratio of the shoulder peak area than the pure CeO₂ and ZrO₂ counterparts. Among these investigated catalysts, the 20Cu/M-Ce80Zr20-50 catalyst possessed the biggest O 1s shoulder peak area ratio, which would further influence the catalytic performance toward CO oxidation reaction. Besides, the specific binding energies of the surface elements of the 20CuO/M-CexZry-500 catalysts were summarized in Table 4. It could be observed that almost all the catalysts displayed greatly similar Cu 2p_{3/2}, Ce 3d_{5/2}, Zr 3d_{5/2}, and O 1s in binding energy values. According to the standard binding energy data, it could be concluded that their main oxidation or valence states were in the form of Cu²⁺, Ce⁴⁺, Zr⁴⁺, and O²⁻, respectively.

3.2.6 CO₂-TPD analysis

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The CO₂-TPD had been widely considered as an effective characterization method for measuring the surface basicity of catalysts. It was widely believed that the basicity of the catalyst was greatly related to the thermal desorption temperature and high desorption temperature usually promised strong basic site.⁶⁴ As shown in Fig. 12, the CO₂-TPD profiles of almost all of the 20CuO/M-CexZry-500 catalysts were similar in shape. It could be seen that the mesoporous Ce-Zr solid solution supported catalysts exhibited a strong CO₂ desorption peak around 153°C. However, the pure mesoporous CeO₂ and ZrO₂ supported catalysts did not show evident CO₂ desorption peak in this temperature region. Therefore, the peak around the 153°C could be partly attributed to

View Article Online the physisorption of CO₂, which was greatly related with textural properties of the catalysts.9/C9CY01612K Compared with the pure CeO_2 and ZrO_2 supported catalysts, the mesoporous Ce-Zr solid solution supported catalysts were provided much higher specific surface areas and bigger pore volumes, accounting for their intense CO_2 desorption peak around 153°C. It was also very interesting to observe that this group of peak were also somewhat related to the Ce/Zr ratio and its intensity gradually increased with the increase of Ce/Zr ratio. Therefore, it could be inferred that the desorption peak could be attributed to both the physisorption and chemisorption of CO_2 on the surface of the material. Furthermore, these catalysts exhibited three additional CO₂ desorption peaks around 253°C, 330°C, and 370°C, which could be ascribed to the medium and strong basic sites. For the two overlapping peaks at 330°C and 370°C, their peak intensities were also closely related to the Ce/Zr ratio of the mesoporous Ce-Zr solid solutions. Specifically, with the gradual increase of the Ce/Zr ratio, the CO₂ desorption amount increased, which intuitively reflected the increase in the basic intensity. However, the desorption peak at 253°C was not very obvious. The results of CO₂ desorption displayed that the basic sites of the mesoporous framework of 20CuO/M-CexZrv-500 catalysts were abundant, especially the peak intensity of 20CuO/M-Ce80Zr20-500 at the corresponding temperature was relatively stronger than other counterparts. It was supposed that the presence of basic sites would be beneficial to the chemical equilibrium shift of the CO oxidation process $(2CO + O_2 \rightarrow 2CO_2)$ by the stabilization of the CO₂ product.

3.3 Catalytic performance for CO oxidation

3.3.1 Catalytic activity

The catalytic activities toward CO oxidation had been carried out over the 20CuO/M-CexZry-500 catalysts with different Ce/Zr ratios, *z*%CuO/M-Ce80Zr20-500 catalysts with different CuO loading amounts, 15CuO/M-Ce80Zr20-T with different calcination temperatures, 20CuO/N-Ce80Zr20-500 with no evident mesostructure, and 15CuO/C-Al₂O₃-600 catalyst with commercial support. Therefore, the effects of Ce/Zr ratio, CuO loading amount, calcination temperature, porous structure, and type of the support on the catalytic performances toward CO oxidation process had been systematically investigated and the results were reflected in Fig. 13.

Fig.13 (1) displayed the catalytic activities over the 20CuO/M-CexZry-500 catalysts 1with P/C9CY01612K different Ce/Zr ratios. Generally, it was noticeable that the CO conversion gradually increased with the increase of the reaction temperature until the CO conversion reached 100%. Apart from this, it was also of great interest to find that the Ce/Zr ratio also greatly affected the catalytic activity of CO oxidation, especially in low reaction temperature region. For instance, the CO conversion *versus* Ce molar percentage (*x*) over 20CuO/M-CexZry-500 catalysts at 80°C was summarized in Fig. 14 (1), which obviously reflected the effect of Ce/Zr ratio on the catalytic activity. With the increase of Ce/Zr ratio, the CO conversion rate gradually increased and reached a maximum peak at Ce molar percentage of 80%. However, further increasing Ce content to 100% would cause the decrease in catalytic activity. Therefore, the 20CuO/M-Ce80Zr20-500 catalyst with the Ce/Zr of 80/20 performed the optimum catalytic activities.

The effect of the CuO loading catalytic amount on the activities over z%CuO/M-Ce80Zr20-500 catalysts was reflected in Fig. 13 (2). The catalytic activity over the M-Ce80Zr20 support without CuO loading was also investigated as a reference. As shown in the figure, it did not show any catalytic activity toward CO oxidation when the reaction temperature was below 110°C. The temperature for 100% conversion of CO over M-Ce80Zr20 was as high as 180°C. Compared with M-Ce80Zr20-500 support, the z%CuO/M-Ce80Zr20-500 catalysts showed much higher catalytic activities, especially in the region of 40-110°C. This indicated that the CuO species was the main active centers for CO oxidation process, which was responsible for the low-temperature oxidation of CO. For instance, the CO conversion versus CuO loading amount over z%CuO/M-Ce80Zr20-500 catalysts at 85°C was displayed in Fig. 14 (2), which obviously reflected the effect of CuO loading amount (z) on the catalytic activity. The catalytic activities of z%CuO/M-Ce80Zr20-500 catalysts gradually could be enhanced with the increase of CuO content up to 15 wt% and 15CuO/M-Ce80Zr20-500 catalyst exhibited the highest catalytic activity, especially in the low reaction temperature region. However, further increasing CuO from 15 wt% to 30 wt% resulted in the decrease of the catalytic activities. The reason for this might be attributed to the poor dispersion of the CuO for the high loading amount. For 15CuO/M-Ce80Zr20-500, the 100% CO conversion could be achieved at 95°C. As a contrast, the temperature for 100% CO over 30CuO/M-Ce80Zr20-500 was 100°C, which was a bit higher than 15CuO/M-Ce80Zr20-500 catalysts.

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Fig. 13 (3) displayed the catalytic performance of 15CuO/M-Ce80Zr20-T catalystsotoward/C9CY01612K CO oxidation, which were calcined at different temperatures. It could be seen that the catalytic activity of the 15CuO/M-Ce80Zr20-T catalysts increased with the calcination temperature from 400°C to 600°C but decreased from 600°C to 700°C. The catalyst calcined at 600°C displayed the best catalytic performances, especially in the low temperature range. The calcination temperature of the catalysts could greatly influence the dispersion over the catalyst surface, textural properties, and the strength of the metal-surface interaction. It could be seen from Fig. 6 (3) that there was some differences in the intensity of CuO diffraction peak of 15CuO/M-Ce80Zr20-T catalysts. Among them, the 15CuO/M-Ce80Zr20-700 exhibited the strongest CuO diffraction peak, indicating the poor dispersion of CuO species. Therefore, the differential catalytic activities of 15CuO/M-Ce80Zr20-T catalysts at different calcination temperatures might be related to the dispersion of CuO active sites. It could be observed that the specific surface areas and pore volumes of the 15CuO/M-Ce80Zr20-T catalysts summarized in Table 2 decreased as the calcination temperature increased. Therefore, the difference in catalytic activity of the 15CuO/M-Ce80Zr20-T catalysts calcined at different temperatures might also be due to the agglomeration of the CuO species and thermal shrinkage of the catalyst frameworks. The high activity of these catalysts were believed to correspond to their excellent mesoporosity, which promised sufficient active centers exposed to the gaseous feedstock and the mass diffusion of CO could be facilitated. As a result, the catalytic activity could be greatly improved.

In order to study the effects of the mesostructure and redox property of the catalytic supports on catalytic activity, the 20CuO/N-Ce50Zr50-500 and 15CuO/C-Al₂O₃-600 were investigated as the reference catalysts of CO oxidation. Their catalytic results toward CO oxidation were shown in Fig. 13 (4). As displayed in the figure, the temperatures for 100% conversion of CO over 20CuO/N-Ce50Zr50-500 (200°C) and 15CuO/C-Al₂O₃-600 (200°C) catalysts were much higher than that over the 20CuO/M-Ce50Zr50-500 mesoporous catalysts, demonstrating the superiority of the mesoporous catalysts.

3.3.2 Long-term stability test

The catalytic stability was also an important concern for CuO based catalysts toward CO oxidation. Therefore, the long term stability test of the z%CuO/M-CexZry-T catalyst was investigated under specific reaction conditions (CO/O₂ = 0.05, GHSV = 12000 mL/(g·h), 100°C, 1

atm) and the 15CuO/M-Ce80Zr20-600 was selected as a representative of the catalyst. $\Phi \text{Cean} = \frac{1}{2} \frac{1}{$

3.3.3 Kinetic study

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In order to further investigate the effects of Ce/Zr ratio, mesostructure, and the redox property of the supports on the activation of the gaseous feed stocks ($CO + O_2$), the kinetic studies were carried out over 20Cu/M-Ce100-500, 20Cu/M-Ce80Zr20-500, 20Cu/M-Ce50Zr50-500, 20Cu/M-Zr100-500, 20Cu/N-Ce50Zr50-500, and 15Cu/C-Al₂O₃-600 representative catalysts. Their Arrhenius plots were exhibited in Fig. 16. It was of great interest to find that the 20Cu/M-Ce80Zr20-500 (89.4 kJ/mol) with 80/20 Ce/Zr ratio displayed much smaller apparent activation energy than 20Cu/M-Ce100-500 (103.3 kJ/mol) and 20Cu/M-Zr100-500 (109.3 kJ/mol) counterparts. This suggested that the catalysts supported on the mesoporous Ce-Zr solid with appropriate Ce/Zr ratio could significantly decrease the activation energy of the CO oxidation reaction. Besides, it could be also observed that the 20Cu/M-Ce50Zr50-500 (102.1 kJ/mol) with mesostructure displayed much lower activation energy than the 20Cu/N-Ce50Zr50-500 (105.1 kJ/mol) without obvious porous structure. The reason for this might be attributed to the facile mass transference of the gaseous feed stocks to the CuO active sites. Furthermore, it was also found that the redox properties of the catalytic supports significantly affected the activation energies of the catalysts. Specifically, the 15CuO/C-Al₂O₃-600 (130.7 kJ/mol) displayed much higher activation energy than the counterparts supported on the Ce-Zr solid solution supports. Overall, the Ce/Zr ratio, mesostructure, and redox property of the support greatly influenced the apparent activation energy of the CO oxidation reaction.

4. Conclusion

A series of mesoporous nanocrystalline Ce-Zr solid solutions with different Ce/Zr ratios were successfully synthesized by EISA strategy. The materials with excellent structural properties could be used as supports of CuO based catalysts for CO oxidation. It was found that the catalysts with 80/20 Ce/Zr ratio, 15 wt% CuO loading amount and 600°C calcination temperature behaved the highest catalytic activity. Compared with the catalyst without obvious mesoporous structure, the

currently synthesized mesoporous catalysts exhibited higher low-temperature catalytic Dactivity;9/C9CY01612K owing to advantageous structural properties. In particular, the mesoporous materials had the characteristics of high specific surface areas, large pore volumes, and uniform pore diameters, which were considered as effective catalyst supports for CO oxidation. In addition, CuO supported on mesoporous Ce-Zr solid solutions could enhance the oxidation activity of CO by synergistic effect between CuO and Ce-Zr solid solutions. The kinetic study also demonstrated that the formation of Ce-Zr solution, mesostructure, and the redox property of the catalytic property contributed to the improvement of the low-temperature catalytic activity by decreasing the apparent energy of the CO oxidation process. Due to these advantageous advantages, mesoporous nanocrystalline Ce-Zr solid solution were considered as a series of promising support for CuO based catalysts toward CO oxidation with enhanced catalytic activity, especially at low temperature.

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Table, and figure captions

Table 1 Physicochemical properties of the catalysts supporter.

 Table 2 Physicochemical properties of the catalysts

Table 3 O 1s peak area of the 20CuO/M-CexZry-500 materials

Table 4 Binding energy (eV) of the surface elements of the 20CuO/M-CexZry-500 materials

Fig. 1 (1) XRD patterns of M-CexZry supports with different Ce/Zr molar ratios calcined at 500°C; (2) XRD patterns of the N-CexZry-500 (x = 50, y = 50) calcined at 500°C and the commercial Al₂O₃ (C-Al₂O₃).

Fig. 2 N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of the catalysts supporter: (1) M-CexZry-500 with different Ce/Zr ratios, (2) N-CexZry-500 (x = 50, y = 50) and C-Al₂O₃.

Fig. 3 TEM and SAED images of the M-CexZry-500 with different Ce/Zr ratios: (a, b, c) M-Ce50Zr50-500, (d, e, f) M-Ce60Zr40-500, (g, h, i) M-Ce80Zr20-500.

Fig. 4 STEM and EDS element mapping images showing the spatial distribution of Ce and Zr elements: **(a)** M-Ce50Zr50-500, **(b)** M-Ce60Zr40-500, **(c)** M-Ce80Zr20-500.

Fig. 5 H₂-TPR profiles of M-CexZry-500 catalyst supports with different Ce/Zr molar ratios

calcined at 500°C.

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Fig. 6 (1) XRD patterns of 20CuO/M-CexZry-500 catalysts with different Ce/Zr molar ratios; (2) XRD patterns of *z*CuO/M-Ce80Zr20-500 catalysts with different CuO loading amounts; (3) XRD patterns of 15CuO/M-Ce80Zr20-T catalysts calcined at different temperatures; (4) XRD patterns of 20CuO/N-Ce50Zr50-500 catalyst without obvious mesostructure and 15CuO/C-Al₂O₃-600 catalyst with commercial γ -Al₂O₃ support.

Fig. 7 N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of catalysts: (1) 20CuO/M-CexZry-500 with different Ce/Zr ratios, (2) z%CuO/M-Ce80Zr20-500 with different CuO content, (3) 15CuO/M-Ce80Zr20-T with different temperature, (4) 20CuO/N-Ce50Zr50-500 and 15CuO/C-Al₂O₃-600.

Fig. 8 TEM and SAED images of 10CuO/M-Ce80Zr20-500 (a, b), 15CuO/M-Ce80Zr20-600 (c, d), 25CuO/M-Ce80Zr20-500 (e, f).

Fig. 9 TEM images of 20CuO/N-Ce50Zr50-500 (a, b, c), 15CuO/C-Al₂O₃-600 (d, e, f).

Fig. 10 (1) H₂-TPR profiles of 20CuO/M-CexZry-500 catalysts with different Ce/Zr molar ratios;
(2) H₂-TPR profiles of *z*CuO/M-Ce80Zr20-500 catalysts with different CuO loading amounts; (3) H₂-TPR profiles of 15CuO/M-Ce80Zr20-T catalysts calcined at different temperatures; (4) H₂-TPR profiles of the 15CuO/C-Al₂O₃-600 and 20CuO/N-Ce50Zr50-500 reference catalysts.

Fig. 11 XPS spectra of Cu 2p (1), Ce 3d (2), Zr 3d (3), and O 1s (4) for 20CuO/M-CexZry-500 materials with different Ce/Zr molar ratios.

Fig. 12 CO₂-TPD profiles of the 20CuO/M-CexZry-500 with different Ce/Zr molar ratios.

Fig. 13 The curves of the CO conversion versus reaction temperature over (1) 20CuO/M-CexZry-500, (2) z%CuO/M-Ce80Zr20-500, (3) 15CuO/M-Ce80Zr20-T, (4) 20CuO/N-Ce50Zr50-500, 20CuO/M-Ce50Zr50-500 and 15CuO/C-Al₂O₃-600; reaction conditions: $CO/O_2 = 0.05$, GHSV = 12000 mL/(g·h), 1 atm.

Fig. 14 The CO conversion versus reaction over (1) 20CuO/M-CexZry-500 (x = 0-1) with different Ce/Zr ratios at 80°C, (2) z%CuO/M-Ce80Zr20-500 (z = 0-30) with different CuO loading at 85°C; reaction conditions: CO/O₂ = 0.05, GHSV = 12000 mL/(g·h), 1 atm.

Fig. 15 Long term stability test over the 15CuO/M-Ce80Zr20-600; reaction conditions:

 $CO/O_2 = 0.05$, GHSV = 12000 mL/(g·h), 100°C, 1 atm.

Fig. 16 Arrhenius plots for the carbon monoxide (CO) reaction rate over the catalysts with

different Ce/Zr ratios, mesostructure, and support.

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Table 1

Samples	Specific Surface Area (m²/g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	Isotherm Type
M-Zr100-500	35.4	0.07	5.6	IV H2
M-Ce20Zr80-500	67.8	0.08	5.6	IV H2
M-Ce40Zr60-500	72.7	0.09	5.6	IV H2
M-Ce50Zr50-500	59.9	0.06	4.9	IV H2
M-Ce60Zr40-500	70.7	0.07	4.9	IV H2
M-Ce80Zr20-500	68.9	0.12	7.9	IV H2
M-Ce100-500	51.8	0.09	4.3	IV H2
C-Al ₂ O ₃	178.3	0.27	4.3	IV H2
N-Ce50Zr50-500	29.3	0.02	3.4	IV H3

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Table 2

Samples	Specific Surface Area Pore Volume		Average Pore Diameter	La di sa Tan
Samples	(m²/g)	(cm ³ /g)	(nm)	isotnerm Type
20CuO/M-Zr100-500	15.2	0.03	5.7	IV H2
20CuO/M-Ce20Zr80-500	46.9	0.07	5.6	IV H2
20CuO/M-Ce40Zr60-500	48.1	0.08	5.6	IV H2
20CuO/M-Ce50Zr50-500	44.5	0.05	4.9	IV H2
20CuO/M-Ce60Zr40-500	42.8	0.06	5.6	IV H2
20CuO/M-Ce80Zr20-500	46.4	0.09	7.8	IV H2
20CuO/M-Ce100-500	12.3	0.06	3.1	IV H2
10CuO/M-Ce80Zr20-500	43.7	0.11	9.6	IV H2
15CuO/M-Ce80Zr20-500	55.2	0.13	9.6	IV H2
25CuO/M-Ce80Zr20-500	47.7	0.11	9.5	IV H2
30CuO/M-Ce80Zr20-500	43.5	0.12	12.4	IV H2
15CuO/M-Ce80Zr20-400	56.3	0.13	9.6	IV H2
15CuO/M-Ce80Zr20-600	33.3	0.12	17.4	IV H2
15CuO/M-Ce80Zr20-700	18.8	0.14	29.9	IV H2
15CuO/C-Al ₂ O ₃ -600	124.4	0.23	5.6	IV H2

4.7	0.01	3.4	
	14.7	0.01	0.01 3.4

Table	3
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Samples	O 1s main peak	O 1s Shoulder peak	O 1s Shoulder peak area ratio	
	area	area	(%)	
20CuO/M-Zr100-500	22049.6	12530.2	36.2	
20CuO/M-Ce20Zr80-500	29263.1	17662.0	37.6	
20CuO/M-Ce40Zr60-500	27839.4	17560.9	38.7	
20CuO/M-Ce50Zr50-500	21288.2	17946.9	45.7	
20CuO/M-Ce60Zr40-500	25905.6	20520.4	44.2	
20CuO/M-Ce80Zr20-500	32862.6	29797.1	47.6	
20CuO/M-Ce100-500	37039.5	9964.0	21.2	

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Table 4

Samples	Cu 2p _{3/2}	O 1s	Ce 3d _{5/2}	Zr 3d _{5/2}
20CuO/M-Zr100-500	933.7	530.0	/	181.9
20CuO/M-Ce20Zr80-500	933.6	529.9	882.8	182.1
20CuO/M-Ce40Zr60-500	933.5	529.9	882.7	182.1
20CuO/M-Ce50Zr50-500	933.7	529.7	882.9	182.2
20CuO/M-Ce60Zr40-500	933.5	529.8	882.6	182.2
20CuO/M-Ce80Zr20-500	933.3	529.8	882.5	181.3
20CuO/M-Ce100-500	933.1	529.5	882.3	/



Fig. 1

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Fig. 2



Fig. 3

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Fig. 5

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Fig. 6

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Fig. 7



Fig. 8







Fig. 10



Fig. 11



Fig. 12



Fig. 13



Fig. 14



Fig. 15



Fig. 16

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The synergistic effect between CuO and mesoporous Ce-Zr solid solution greatly enhanced the advanced low-temperature catalytic activity toward CO oxidation.