



Ordered Mesoporous CeO₂-supported Ag as an Effective Catalyst for Carboxylative Coupling Reaction Using CO₂

Xiao Zhang,^{*,[a]} Dingkun Wang,^[a] Meizan Jing,^[a] Jian Liu,^{*,[a]} Zhen Zhao,^{*,[a]} Guanhua Xu,^[a] Weiyu Song,^[a] Yuechang Wei,^[a] and Yuanqing Sun^[a]

Ag/Mesoporous CeO₂ (Ag/M–CeO₂) catalysts were synthesized through the gas bubbling-assisted membrane reduction (GBMR) method and characterized by XRD, ICP-OES, N₂ adsorption-desorption, XPS, Raman spectroscopy, TEM, HRTEM, HAADF-STEM and CO₂-TPD. Ag/M–CeO₂ catalysts contain uniform mesoporous structure, large surface area and oxygen vacancies, which promote the dispersion of Ag nanoparticles. Density functional theory (DFT) calculations indicate that Ag nano-

particles supported on M–CeO₂ could facilitate the formation of oxygen vacancies, which result in higher CO₂ adsorption capacity. With the most oxygen vacancies and the well-dispersed Ag active species, Ag (3.12%)/M–CeO₂ exhibits high efficiency for the carboxylative coupling of terminal alkynes, chloride compounds and CO₂ under mild reaction conditions (60 °C, 0.5 MPa), affording a wide range of functionalized 2-alkynoates in good yields.

Introduction

During the last few decades, the excessive CO₂ emission from fossil energy conversion has caused global warming and climate change, which should be dealt with greatest attention.^[1] On the other hand, CO₂ is an important C1 source in organic synthesis owing to its nontoxicity, renewability and accessibility.^[2] Thus, the exploitation of CO₂ chemical transformations to high-value products is identified as an attractive approach to control and reduce CO₂ emissions. To date, many efforts have been devoted towards CO₂-involved synthesis of useful chemicals.^[3] Among them, the synthesis of functionalized 2-alkynoates through the carboxylative coupling of terminal alkynes, organohalides and CO₂ has attracted much attention,^[4] because the products are key intermediates in the synthesis of a variety of pharmaceutically important compounds and fine chemicals.^[5] Generally, several homogeneous catalytic systems including transition-metal salts and complexes (e.g. Cu^[6] and Ag^[7]) have been developed for this reaction. Nevertheless, most of these methods have the problems of the separation and recovery of the metal. In the effort to develop sustainable processes, a few heterogeneous catalysts have been introduced in this reaction. For instance, CuBr loaded on activated carbon,^[8] CuCl₂ incorporated in polyvinyl imidazolium tri-cationic ionic liquid,^[9] Cu nanoparticles supported on Al₂O₃,^[10] and Ag nanoparticles encapsulated in the porphyrin MOF^[11] displayed excellent catalytic activities for the carboxylative coupling reaction. However, due to the thermodynamic and kinetic

stability of CO₂, the transformation of CO₂ to functionalized 2-alkynoates using heterogeneous catalysts under mild reaction condition remains a great challenge.

Recently, M–CeO₂ served as supporting material has attracted great interest in the catalysis.^[12–15] The well-regularized mesoporous structure of M–CeO₂ not only increases the specific surface that improves the dispersion of metal nanoparticles,^[16–18] but also facilitates the transport of reactants through the material.^[19,20] For example, Zhou et al. reported that Ni/M–CeO₂ showed excellent catalytic activity for CO₂ methanation. Owing to the high specific surface area and ordered mesoporous structure, Ni active species could be highly dispersed on M–CeO₂. Moreover, Ni/CeO₂ possesses oxygen vacancies which can effectively promote CO₂ activation.^[21]

Herein, inspired by the previous works, we synthesized M–CeO₂ by the hard-template method and loaded different amounts of Ag to yield Ag/M–CeO₂ through the GBMR method. A variety of terminal alkynes, chloride compounds and CO₂ are catalyzed by Ag (3.12%)/M–CeO₂, affording the corresponding products in good yields (74–91 %) under mild reaction condition (60 °C, 0.5 MPa). In addition, Ag (3.12%)/M–CeO₂ shows good stability and recyclability.

Results and Discussion

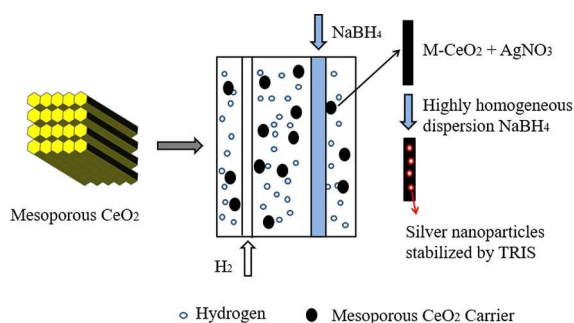
M–CeO₂ was synthesized using KIT-6 as hard template.^[22] Ag/M–CeO₂ catalyst was synthesized by the GBMR method. The schematic diagram of the GBMR method is presented in Scheme 1.

Ag/M–CeO₂ which have Ag loading of 1.33 %, 3.12 %, and 5.24 % were confirmed by ICP-OES analysis. The wide-angle XRD patterns of bulk CeO₂ (B–CeO₂) synthesized without the addition of hard template, mesoporous CeO₂ (M–CeO₂) and Ag/M–CeO₂ are illustrated in Figure 1a. The distinct diffraction peaks at 2 θ = 28.6°, 33.0°, 47.4°, 56.3°, 69.5° and 76.8° are all indexed to a cubic fluorite structure of CeO₂ (space group

[a] Prof. X. Zhang, D. Wang, M. Jing, Prof. J. Liu, Prof. Z. Zhao, G. Xu, Prof. W. Song, Prof. Y. Wei, Dr. Y. Sun
College of Science, State Key Laboratory of Heavy Oil Processing
China University of Petroleum-Beijing
18 Fuxue Road, Changping, Beijing (China)
E-mail: zhangxiao@cup.edu.cn
liujian@cup.edu.cn
zhenzhao@cup.edu.cn

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.201900039>

Fm3 m, JCPDS 34–0394) and could be corresponding to the (111), (200), (220), (311), (400) and (331) crystal planes. Compared with the pure M–CeO₂, the wide-angle XRD patterns of Ag/M–CeO₂ show an additional peak at $2\theta = 38.2^\circ$, associated with (111) plane of Ag face centered cubic (fcc) phase (JCPDS 65–2871). There is only one weak diffraction peak attributable to Ag, implying that Ag nanoparticles are homogeneously distributed on M–CeO₂.^[12] The mean sizes of Ag nanoparticles are estimated using Scherrer equation from line broadening of the Ag (111) plane in the wide angle XRD patterns (Figure 1a).^[23,24] The mean sizes of Ag nanoparticles in Ag (1.33%)/M–CeO₂, Ag (3.12%)/M–CeO₂ and Ag (5.24%)/M–CeO₂ are 6.6, 6.5 and 7.1 nm, respectively. The small angle XRD patterns of all mesoporous samples are shown in Figure 1b. The characteristic



Scheme 1. Preparation of Ag/M–CeO₂ by the GBMR method.

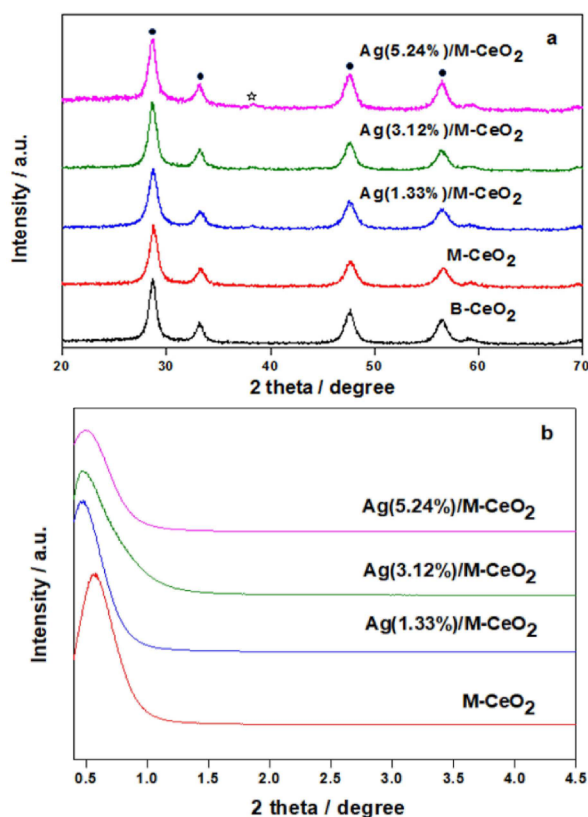


Figure 1. (a) Wide angle XRD; (b) Small angle XRD.

peak at 2θ of around 0.6° can be clearly observed, ascribed to the (211) diffraction peak of the cubic Ia3d symmetry of mesoporous silica template. These results indicate that both M–CeO₂ and Ag/M–CeO₂ could maintain the same regular mesostructures as the KIT-6 plates.

To detect pore properties and the surface area of B–CeO₂, M–CeO₂ and Ag/M–CeO₂, N₂ adsorption-desorption measurements were carried out at -196°C . As shown in Figure 2, in accordance with IUPAC classification, N₂ adsorption-desorption isotherms of all prepared samples can be classified as type IV isotherm. B–CeO₂ shows a hysteresis loop in the medium and high-pressure region ($P/P_0 = 0.7\text{--}1.0$), which attributes to type H2. For M–CeO₂, the hysteresis loop with the relative pressure ranges ($P/P_0 = 0.75\text{--}1.0$) is verified to type H4, indicating the formation of mesopore structures. Ag/M–CeO₂ with different amounts of Ag nanoparticles exhibit similar rising isotherms within a relative pressure range from 0.4–0.6, which corresponds to the capillary condensation of the mesopores. The rising curves at a relative pressure of 0.8–1.0 reflect that Ag/M–CeO₂ possesses the mesopore structure. The pore size distribution (PSD) profiles of M–CeO₂ and Ag/M–CeO₂ based on BJH method (Fig. 2b) also show a typical mesoporous structure of the material, and the pore sizes are ca. 4 nm. The surface area, pore volume and average pore size of B–CeO₂, M–CeO₂ and Ag/M–CeO₂ are summarized in Table S1. The surface areas of

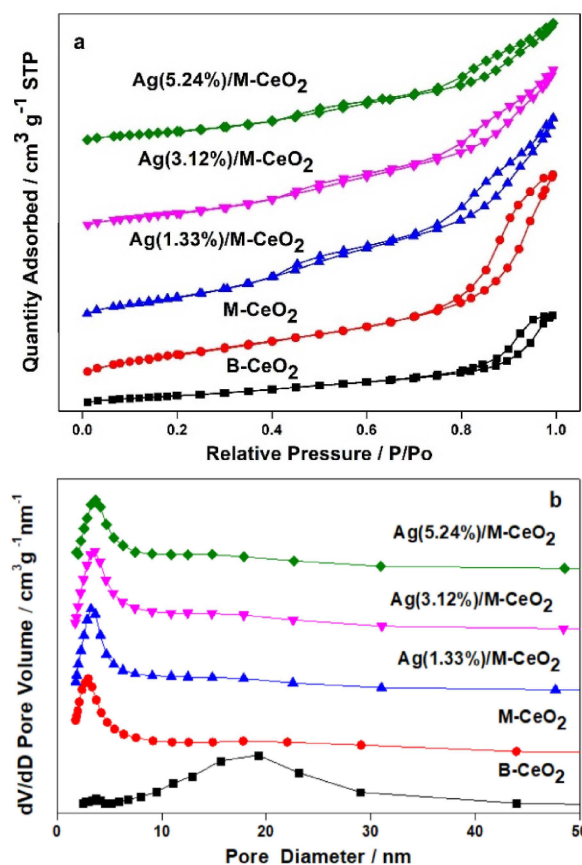


Figure 2. (a) N₂ adsorption-desorption isotherms of B–CeO₂, M–CeO₂ and Ag/M–CeO₂; (b) Pore Diameter distribution.

B-CeO₂, M-CeO₂, Ag (1.33%)/M-CeO₂, Ag (3.12%)/M-CeO₂, Ag (5.24%)/M-CeO₂ are 78, 154, 145, 144, and 142 m²/g, respectively. Due to the well-ordered mesoporous and interconnected channels of M-CeO₂, the BET surface area of M-CeO₂ is much higher than that of B-CeO₂. What's more, the pore volume of M-CeO₂ (0.42 cm³/g) is larger than that of B-CeO₂ (0.15 cm³/g). M-CeO₂ could promote the dispersion of Ag nanoparticles^[25] and make the reactants diffusion facile^[26] with high surface area and large pore volume. With the increasing of Ag loading amounts, the BET surface area, pore volume and average pore size slightly decrease (Table S1).

The surface composition and chemical state of different elements were examined using XPS analysis in these samples, Figure 3a presents the XPS spectra of Ce 3d, O 1s and Ag 3d for Ag/M-CeO₂ samples, and Ce 3d, O 1s for M-CeO₂ sample. For M-CeO₂ and Ag/M-CeO₂, it can be found that the Ce 3d level has a rather complex structure and the spectrum can be separated into ten peaks (u₁, u₂, u₃, u₄, u₅, v₁, v₂, v₃, v₄, v₅) with u and v referring to Ce 3d_{3/2} and Ce 3d_{5/2} components (Figure 3b). The peaks labelled u₁, u₂, u₄, v₁, v₂, and v₄ are characteristic of Ce⁴⁺, while u₃, v₃, u₅, and v₅ are assigned to Ce³⁺. As shown in Table S2, the calculated surface concentrations of Ce³⁺ for M-CeO₂, Ag (1.33%)/M-CeO₂, Ag (3.12%)/M-CeO₂, Ag (5.24%)/M-CeO₂ are 18.0, 28.3, 38.1, and 32.2%, respectively. The amounts of Ce³⁺ increase with the addition of Ag nanoparticles on M-CeO₂, suggesting that the interaction between Ag nanoparticles and CeO₂ contributes to a partial Ce⁴⁺ → Ce³⁺ reduction. It has been reported that the formation of oxygen vacancies is ascribed to the partial reduction of Ce⁴⁺ to Ce³⁺.^[27,28] Ag (3.12%)/M-CeO₂ has the highest content of Ce³⁺, producing the most oxygen vacancies, which can facilitate the dispersion of Ag nanoparticles.^[12] According to Figure 3c, three kinds of peaks can be identified by the deconvolution of the O1s spectra. The peak of O at the lowest binding energy is attributed to O²⁻ in the CeO₂ lattice, the second one with the middle binding energy is due to the chemisorbed oxygen O₂²⁻ and the third one at the highest binding energy is assigned to the adsorbed molecular water or surface hydroxyl species. It is established that O₂²⁻ species are produced by oxygen adsorption on the surface defects of ceria^[29] and the ratio of the chemisorbed oxygen can be used to evaluate the concentration of the oxygen vacancies.^[30,31] As shown in Table S2, the ratio of the chemisorbed oxygen O₂²⁻ decreases in the order of Ag (3.12%)/M-CeO₂ (36.5%) > Ag (5.24%)/M-CeO₂ (27.0%) > Ag (1.33%)/M-CeO₂ (25.9%) > M-CeO₂ (22.8%). These results show that the incorporation of Ag on M-CeO₂ enhances the amounts of oxygen vacancies and Ag (3.12%)/M-CeO₂ has the highest content of oxygen vacancies. The Ag 3d spectra (Figure 3d) give peaks at binding energies of 368.5 eV (3d_{5/2}) and 374.5 eV (3d_{3/2}) with the spin energy separation of 6.0 eV which are assigned to metallic Ag nanoparticles.^[12,32]

Raman spectra of M-CeO₂ and Ag/M-CeO₂ catalysts are shown in Figure 4. All these samples exhibit two main Raman adsorption peaks, an intense peak located at 460 cm⁻¹ and a weak peak at 596 cm⁻¹. The peak around 460 cm⁻¹ is assigned to the strong F_{2g} vibration mode.^[33,34] Another weak peak is ascribed to defect-induced (D) mode.^[35] According to the

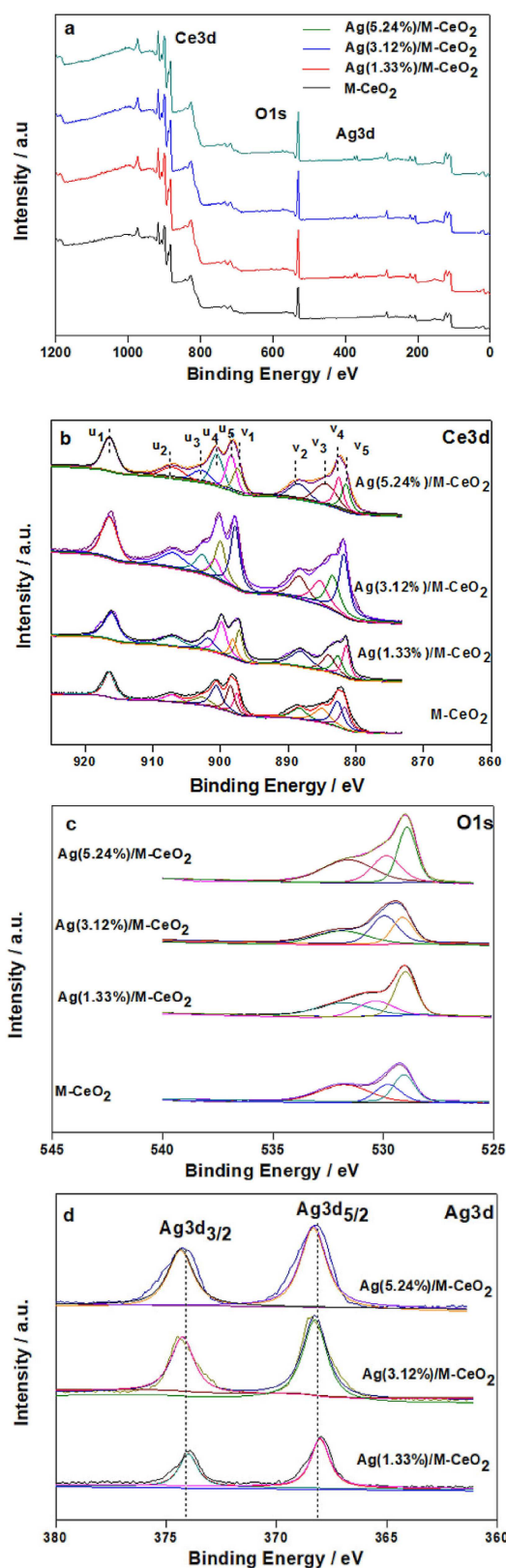


Figure 3. XPS spectra of M-CeO₂ and Ag/M-CeO₂: (a) survey XPS spectrum; (b) Ce 3d; (c) O 1s; (d) Ag 3d.

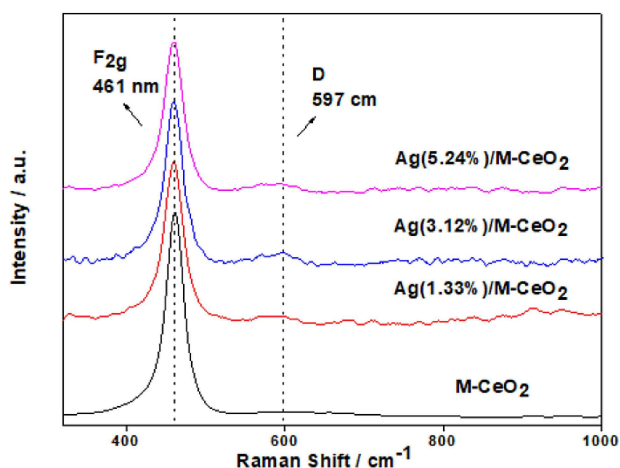


Figure 4. Raman spectra of M-CeO₂ and Ag/M-CeO₂.

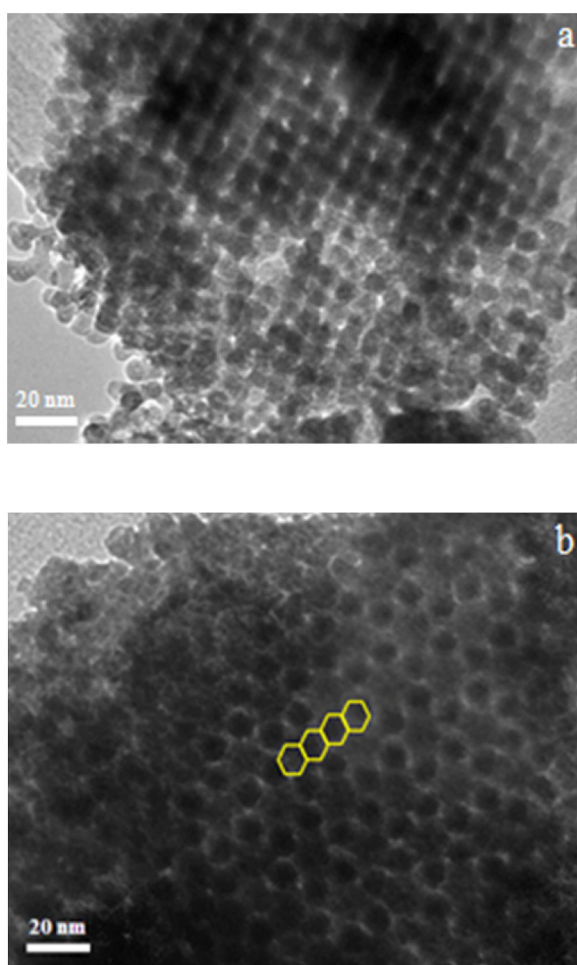


Figure 5. TEM images of M-CeO₂.

peaking fitting of the D and F_{2g} modes in the Raman spectra, we can calculate the ratio of I_D/I_{F2g} , representing the relative content of oxygen defect sites.^[25,34] The I_D/I_{F2g} values of M-CeO₂, Ag (1.33%)/M-CeO₂, Ag (3.12%)/M-CeO₂, and Ag (5.24%)/

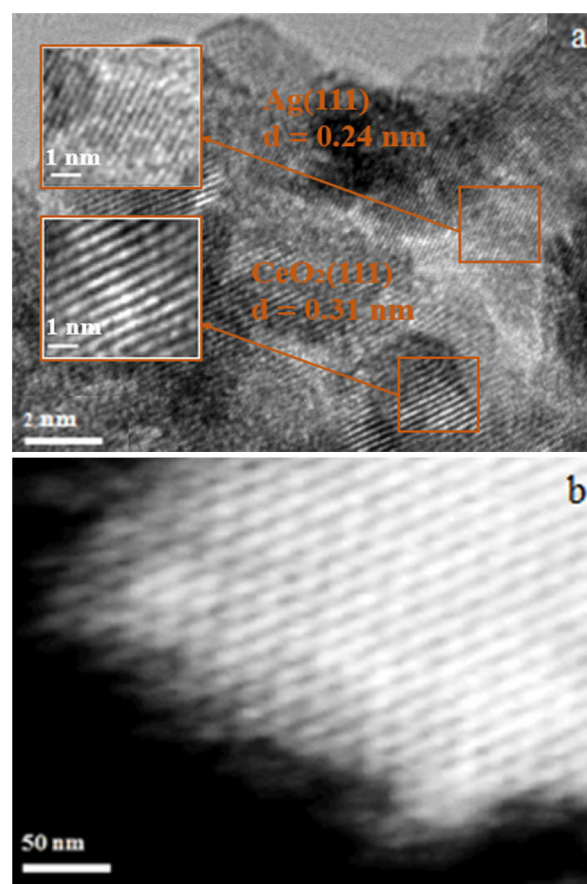


Figure 6. (a) HRTEM image of Ag (3.12%)/ M-CeO₂; (b) HAADF-STEM image of Ag (3.12%)/ M-CeO₂.

M-CeO₂ are 2.57%, 3.53%, 7.87%, and 5.60%, respectively. Therefore, supported Ag nanoparticles on M-CeO₂ could increase the oxygen vacancies, and Ag (3.12%)/M-CeO₂ has the most oxygen vacancies.

The TEM images of M-CeO₂ are shown in Figure 5. M-CeO₂ displays highly ordered mesoporous structures, which indicate that M-CeO₂ contains a perfect replica structure of KIT-6 template.

HRTEM image of Ag (3.12%)/M-CeO₂ in Figure 6a shows the lattice fringes ($d = 0.31$ nm) corresponding to the (111) crystallographic planes of CeO₂, and the lattice spacing value of 0.24 nm is assigned to the (111) crystallographic planes of the metal Ag.^[36,37] These results are consistent with the ones observed from XRD characterization. In the HAADF-STEM image of Ag (3.12%)/M-CeO₂ (Figure 6b), the regular mesoporous structure and well-arranged morphology are not changed after loading Ag nanoparticles. The element distribution of Ag (3.12%)/M-CeO₂ is obtained using EDS elemental mapping analysis. As shown in Figure 7, it can be found that the Ce and Ag are well distributed throughout Ag/M-CeO₂.^[25]

Figure 8 shows the CO₂-TPD curves of M-CeO₂, Ag (1.33%)/M-CeO₂, Ag (3.12%)/M-CeO₂ and Ag (5.24%)/M-CeO₂. For all these samples, the desorption of CO₂ occurs in two temperature regions of 50–200 and 320–460 °C. Calculated based on the

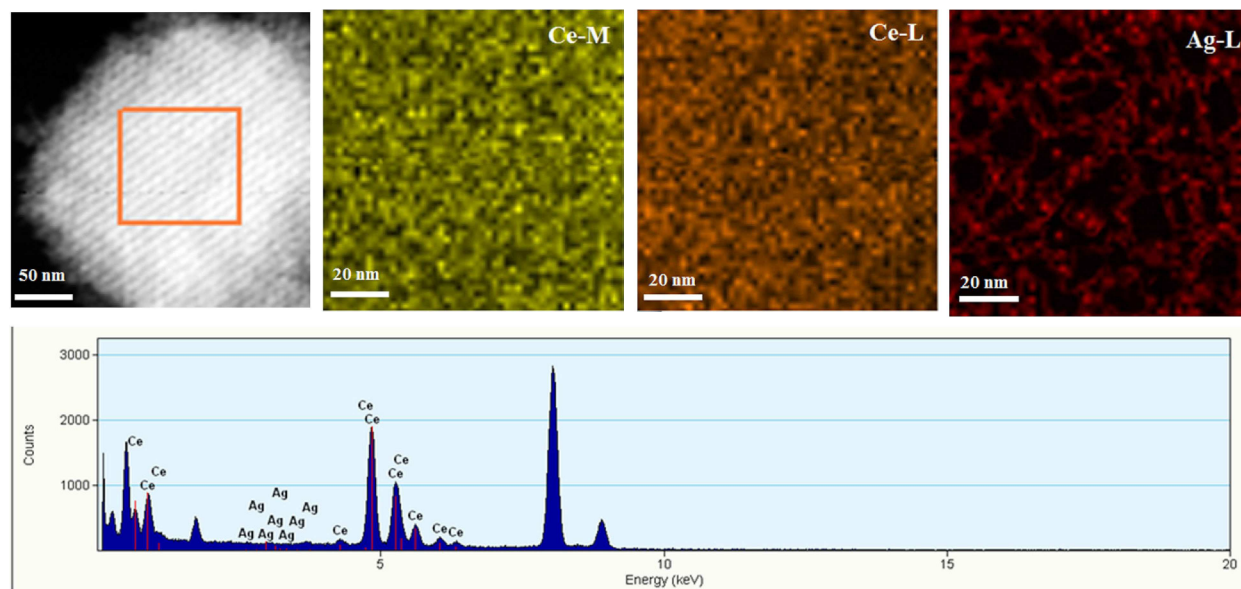


Figure 7. EDS elemental mapping of Ag (3.12%)/M-CeO₂.

curves in Figure 8, the amounts of desorbed CO₂ are shown in Table S3. The total amounts of desorbed CO₂ follow the order: Ag (3.12%)/M-CeO₂ (0.70 mmol g⁻¹) > Ag (5.24%)/M-CeO₂ (0.59 mmol g⁻¹) > Ag (1.33%)/M-CeO₂ (0.50 mmol g⁻¹) > M-CeO₂ (0.44 mmol g⁻¹), and the total amounts of adsorbed CO₂ follow the same order.^[38,39] It is noted that the order of CO₂ adsorption ability of the samples is in accordance with the concentration of oxygen vacancies. The result shows that oxygen vacancies could promote CO₂ adsorption.

The CO₂ adsorption on the stoichiometric CeO₂(111), the reductive CeO₂(111), the stoichiometric Ag_n/CeO₂(111) and the reductive Ag_n/CeO₂(111) were theoretically investigated by DFT calculations.

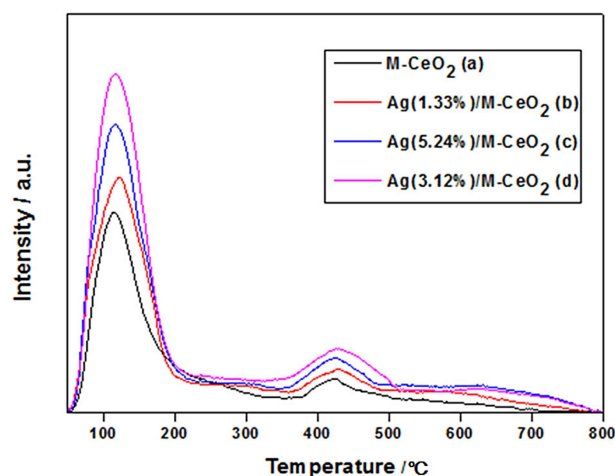


Figure 8. CO₂-TPD of (a) M-CeO₂, (b) Ag(1.33%)/M-CeO₂, (c) Ag(5.24%)/M-CeO₂, (d) Ag(3.12%)/M-CeO₂.

We chose the CeO₂(111) surface, the most stable surface termination,^[40] which consists of 9 atomic layers (three O-Ce-O trilayers) with a 3×3 unit cell (Figure 9a). The vacuum space that perpendicular to the surface is set to 15 Å in order to minimize the interaction between distinct slab surfaces. During geometry optimization, the top six atom layers of ceria are relaxed, while bottom three layers are fixed in their bulk positions. The CeO₂-supported Ag nanorod system is modeled by adding a two-layer Ag nanorod on the top of the stoichiometric CeO₂(111) surface (shown in Figure 9b),^[41,42] which is denoted as Ag_n/CeO₂(111) (where n represents the nanorod).

On the stoichiometric CeO₂ (111) surface (Figure 10a), CO₂ can be adsorbed with low adsorption energy of -0.04 eV (C terminal adsorption) or -0.07 eV (O terminal adsorption). More-

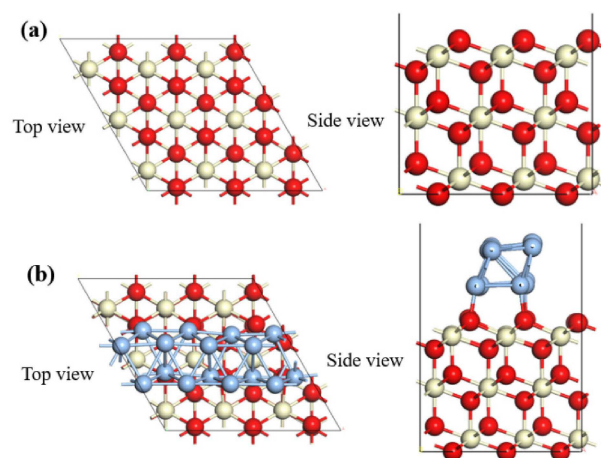


Figure 9. Top and side views of (a) CeO₂(111) and (b) Ag_n/CeO₂(111). (White and red spheres represent Ce and O atom, respectively)

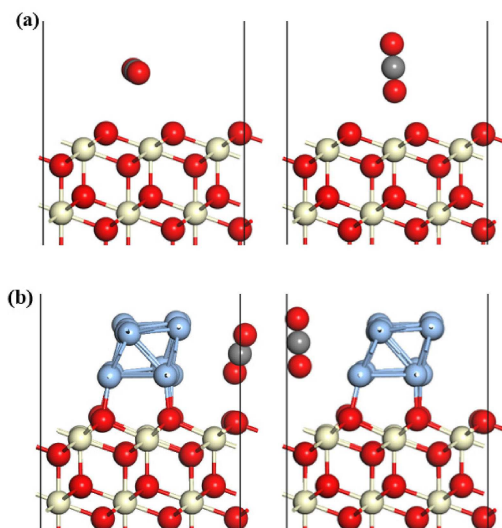


Figure 10. The optimized structures of CO₂ adsorptions on (a) stoichiometric CeO₂(111) and (b) Ag_n/CeO₂(111). (Black spheres represent C atom.)

over, on the stoichiometric Ag_n/CeO₂(111) surface (Figure 10b), the interface between Ag and CeO₂ has no effect on CO₂ adsorption, which can be proved by the low adsorption energy (−0.05 eV or −0.13 eV).

Due to the outstanding redox ability of CeO₂, it's very common that there are large numbers of oxygen vacancies on CeO₂(111) and Ag_n/CeO₂(111) surface.^[15–18] Three types of oxygen vacancies (O-1 type, O-2 type, and O-3 type) can be formed on Ag_n/CeO₂(111) surface (Figure 11). O-1 type loses oxygen atom on the ceria surface, while O-2 type and O-3 type lose oxygen atom lie in the interface of Ag nanorod and CeO₂ support. Among them, O-1 type owns the low oxygen vacancy formation energy ($E_{ov} = 2.27$ eV) (Figure 11b). However, O-2 type and O-3 type oxygen vacancies in interface are difficult to generate ($E_{ov} = 2.41$ eV) because the distortion of structure

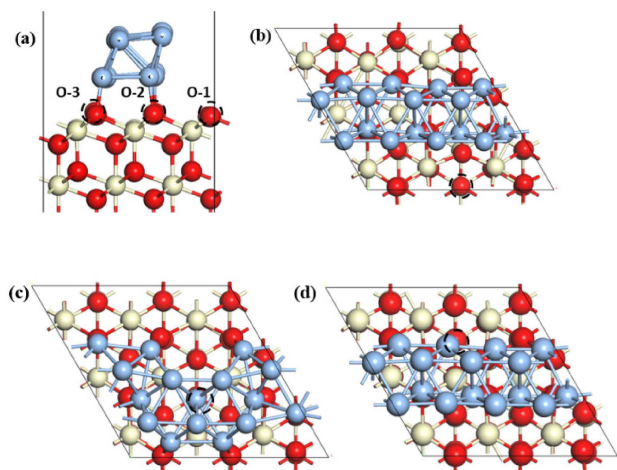


Figure 11. Oxygen vacancy formations on different O sites of Ag_n/CeO₂(111). (a) Stoichiometric Ag_n/CeO₂(111), (b) Reductive Ag_n/CeO₂(111)-Ov1, (c) Reductive Ag_n/CeO₂(111)-Ov2, (d) Reductive Ag_n/CeO₂(111)-Ov3.

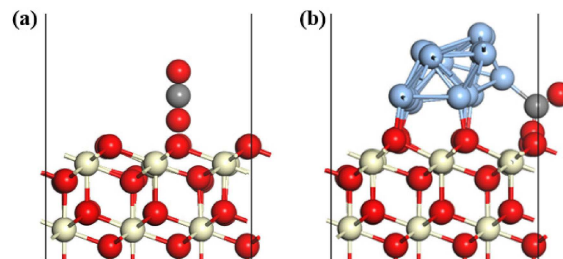


Figure 12. The optimized structures of CO₂ adsorptions on (a) reductive CeO₂(111) and (b) reductive Ag_n/CeO₂(111).

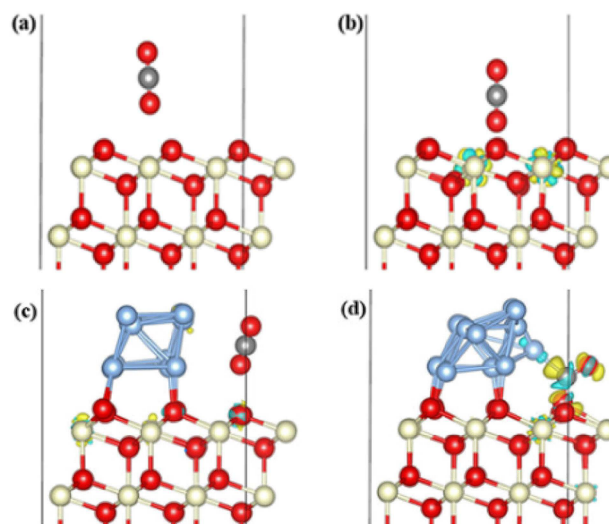


Figure 13. Calculated charge density difference of CO₂ adsorptions on (a) CeO₂(111), (b) reductive CeO₂(111), (c) Ag_n/CeO₂(111) and (d) reductive Ag_n/CeO₂(111) (yellow and blue isosurfaces represent increasing and decreasing electron densities, respectively).

(Figure 11c and 11d). Therefore, we choose O-1 type oxygen vacancies on the reductive Ag_n/CeO₂(111) surface. Compared with the oxygen vacancy formation energy on CeO₂(111) ($E_{ov} = 2.39$ eV) and Ag_n/CeO₂(111) ($E_{ov} = 2.27$ eV) surface, the Ag nanorod contributes to the formation of oxygen vacancy on ceria surface.

On the reductive CeO₂ (111) surface, CO₂ can be adsorbed on this reductive surface with the energy of −0.26 eV (Figure 12a). Compared to the low CO₂ adsorption energy of −0.04 eV on the stoichiometric CeO₂ (111) surface, the presence of oxygen vacancies in reducible support provides the site for CO₂ adsorption.^[43,44] On the reductive Ag_n/CeO₂(111) surface, CO₂ can be strongly adsorbed with the energy of −1.08 eV. It can be found that oxygen vacancies are beneficial for CO₂ adsorption. The adsorption structure is shown in Figure 12b. O atom makes up the oxygen vacancy and is connected with Ce atom, while the C atom is connected with Ag atom.

These results can be further supported by the differences of the calculated charge densities of CO₂ adsorption. As shown in Figure 13(a–c), whether on the stoichiometric CeO₂(111) surface, reductive CeO₂(111) surface or stoichiometric Ag_n/CeO₂(111)

Table 1. Synthesis of cinnamyl phenylpropiolate from phenylacetylene (1a), CO₂, and cinnamyl chloride (2a) with catalysts.^[a]

$\text{Ph}-\text{C}\equiv\text{CH} + \text{CO}_2 + \text{Ph}-\text{CH}=\text{CH}-\text{CH}_2\text{Cl} \longrightarrow \text{Ph}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{Ph}$				
Entry	Catalyst [mg]	Base	Solvent	Yield [%] ^[b]
1	Ag(1.33%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	81
2	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	91
3	Ag(5.24%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	90
4	Ag(3.12%)/M–CeO ₂ (100)	Cs ₂ CO ₃	DMF	83
5	Ag(3.12%)/M–CeO ₂ (140)	Cs ₂ CO ₃	DMF	91
6	–	Cs ₂ CO ₃	DMF	4.2
7	M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	18
8	Ag(3.12%)/M–CeO ₂ (120)	K ₂ CO ₃	DMF	33
9	Ag(3.12%)/M–CeO ₂ (120)	CsOAc	DMF	58
10	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMSO	80
11	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	THF	45
12 ^[c]	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	80
13 ^[d]	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	91
14 ^[e]	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	62
15 ^[f]	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	91
16 ^[g]	Ag(3.12%)/M–CeO ₂ (120)	Cs ₂ CO ₃	DMF	0

[a] Reaction conditions: phenylacetylene (1a) (1.0 mmol), cinnamyl chloride (1.5 mmol) (2a), catalyst, base (2.0 mmol), CO₂ (0.5 MPa), 60 °C, solvent (5 mL), 24 h. [b] Isolated yield. [c] 20 h. [d] 28 h. [e] CO₂ (balloon) [f] 1.0 MPa. [g] In the absence of CO₂.

surface, there is no charge transfer between CO₂ and corresponding catalysts. However, it can be seen in Figure 13d that there is significant charge transfer between CO₂ and reductive Ag_n/CeO₂(111) support. So, both the oxygen vacancies and Ag–Ce interface can influence the CO₂ adsorption.

The catalytic activities of Ag/M–CeO₂ are evaluated by the carboxylative coupling reaction of phenylacetylene (1a), CO₂, and cinnamyl chloride (2a) (Table 1). It is found that 120 mg three kinds of catalysts and 2.0 equiv. Cs₂CO₃, give good yields of cinnamyl phenylpropiolate (3a) (entries 1–3). Ag (3.12%)/M–CeO₂ represents the best catalytic performance (entries 2), which may be attributed to the well dispersion of Ag nanoparticles and the most oxygen vacancies. CO₂-TPD and DFT studies have demonstrated that oxygen vacancies are beneficial for CO₂ adsorption. Moreover, it has been reported that oxygen vacancies can promote CO₂ activation.^[27,28,45] When the amount of Ag (3.12%)/M–CeO₂ is decreased to 100 mg, the yield decreases to 83% (entries 4). 140 mg Ag (3.12%)/M–CeO₂ gives the same yield of cinnamyl phenylpropiolate (91%) (entries 5). The yield could not be further improved by increasing the amount of catalyst. It is noteworthy that almost no carboxylative coupling product is observed in the absence of any catalyst (entry 6). M–CeO₂ shows certain catalytic activity for the reaction (entry 7). The yield (18%) is higher than that (4.2%) without any catalyst (entries 7 and 6). The catalytic activity of M–CeO₂ can be attributed to the presence of oxygen vacancies on M–CeO₂.^[27,28,45] But the yield is much lower than that (91%) when Ag (3.12%)/M–CeO₂ is used as the catalyst (entries 7 and 2), suggesting that Ag nanoparticles play an important role in carboxylative coupling reaction.

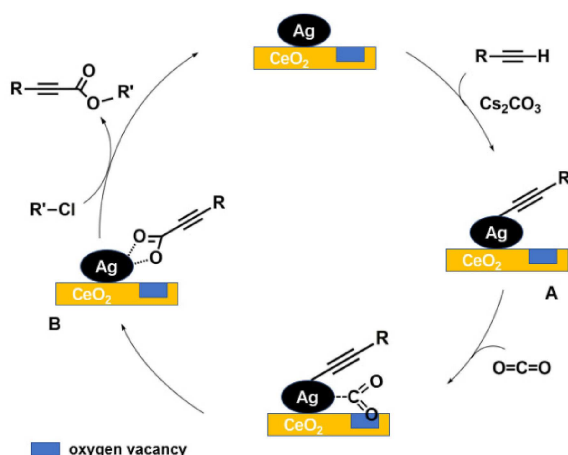
Table 2. Ag(3.12%)/M–CeO₂ catalyzed the carboxylative coupling reaction of terminal alkynes (1), CO₂, and chloride compounds (2).^[a]

$\text{R}-\text{C}\equiv\text{CH} + \text{CO}_2 + \text{R}'-\text{CH}_2\text{Cl} \longrightarrow \text{R}-\text{C}\equiv\text{C}-\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{R}'$			
Entry	Terminal Alkynes	Chloride Compounds	Yield [%] ^[b]
1	(1b)	(2a)	90
2	(1c)	(2a)	91
3	(1d)	(2a)	84
4	(1e)	(2a)	81
5	(1a)	(2b)	74
6	(1a)	(2c)	75
7	(1a)	(2d)	83
8	(1a)	(2e)	81
9	(1a)	(2f)	85

[a] Reaction conditions: Alkyne (1.0 mmol), chloride compounds (1.5 mmol), Ag(3.12%)/M–CeO₂ (120 mg), Cs₂CO₃ (2.0 mmol), CO₂ (0.5 MPa), DMF (5 mL), 60 °C, 24 h. [b] Isolated yield.

In order to recognize the efficient reaction conditions for promoting the carboxylative coupling, the reaction is under various reaction times with different bases and solvents (Table 1, entries 8–11). In the base screening, Cs₂CO₃ is the best base for this reaction (entries 8 and 9). It is confirmed that DMF is a superior solvent in comparison with THF and DMSO, because DMF is a weak base which is a better solvent for CO₂ (entries 10 and 11).^[46] Besides, we carried out the catalytic reactions for different durations ranging from 20 h to 28 h. It is found that after 24 h the optimum conversion has been achieved (entries 2, 12 and 13). The influence of CO₂ pressure on the reaction is also studied (entries 14 and 15), and the highest yield is obtained under the CO₂ pressure (0.5 MPa). It is worthwhile noting that no carboxylative coupling product is observed when the reaction proceeds in the absence of CO₂ (entry 16), showing that the CO₂ unit in carboxylative coupling product comes from free CO₂, rather than the carbonate salts.

With the optimized conditions (2.0 equiv. Cs₂CO₃, 0.5 MPa CO₂, DMF, 60 °C, 24 h) in hand, various aryl-substituted terminal alkynes smoothly undergo the carboxylative coupling reaction (Table 2, entries 1–4). Both electron-donating group (CH₃ and ^tBu) and electron-withdrawing (Br and F) group substituted phenylacetylenes successfully converted into the corresponding



Scheme 2. Mechanism proposed for carboxylative coupling reaction by Ag/M-CeO₂

products in good yields. Furthermore, allylic chlorides, propargylic chlorides and aryl halides are tested under the optimized conditions (entries 5–9), showing high yields of the corresponding products. Thus, this novel catalytic system shows wide generality for the synthesis of various functionalized 2-alkynoates.

We examined the reusability of Ag(3.12%)/M-CeO₂ catalyst in the reaction. Ag(3.12%)/M-CeO₂ catalyst was recovered from the reaction solution by centrifugation. Then the solid residue was directly used as recycled catalyst in the subsequent runs without the addition of more catalyst. In Figure 14, Ag(3.12%)/M-CeO₂ catalyst can be recovered and reused five times without visible loss in catalytic activities. The loading of Ag in the used catalysts after five catalytic cycles is 3.08% as monitored by ICP-OES, and the loading of Ag in the fresh catalyst is 3.12%, which recommends that there is no obvious leakage of Ag. The XRD patterns and N₂ adsorption-desorption (Figures S1 and S2) of the reused catalyst do not exhibit any obvious changes, which indicates that the spatial structure and

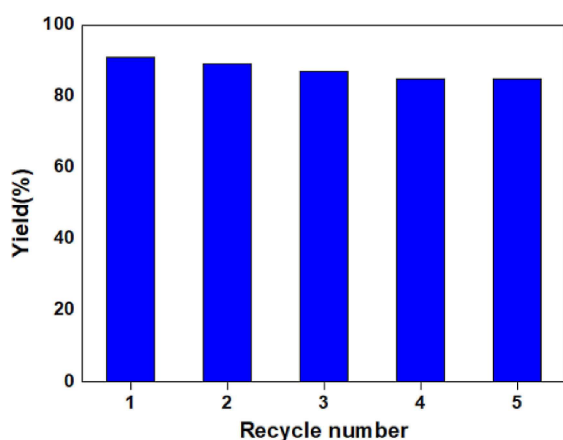


Figure 14. Recovery and reuse of Ag(3.12%)/M-CeO₂

regular ordered mesopores have not been destroyed during the process of the reaction.

On the basis of the experimental results, DFT calculations and previous reports,^[6–11] a plausible reaction mechanism for the carboxylative coupling reaction is proposed in Scheme 2. Firstly, Ag nanoparticles of Ag/M-CeO₂ can coordinate terminal alkynes with Cs₂CO₃ to form silver acetylide intermediate A. Some reports have demonstrated that Ag nanoparticles supported on the organic network polymers,^[47] Schiff base,^[48] MOF^[46,49] and metal oxides,^[50] which can coordinate and activate terminal alkynes in the carboxylation of terminal alkynes with CO₂. Meanwhile, CO₂ is adsorbed and activated on the oxygen vacancies.^[27,28,45] Then, the insertion of CO₂ into the nearby silver acetylide generates the silver carboxylate intermediate B. Finally, chloride compounds react with the intermediate B forming the product, and simultaneously release the catalyst to fulfill the cycle.

Conclusions

In this work, highly ordered mesoporous Ag/M-CeO₂ catalysts were prepared by the GBMR method. Ag/M-CeO₂ contains more oxygen vacancies than M-CeO₂. CO₂-TPD and the DFT calculations indicate that the Ag nanoparticles induce the increase of oxygen vacancies, which contribute to CO₂ adsorption. Ag (3.12%)/M-CeO₂ can catalyze the carboxylative coupling reaction of terminal alkynes, chloride compounds and CO₂, which provides a convenient approach to straightforwardly synthesize various functionalized 2-alkynoates in good yields (74–91%) under mild conditions (60 °C, 0.5 MPa). In addition, Ag (3.12%)/M-CeO₂ can be readily recovered and reused for five times without significant decrease in catalytic activity.

Experimental Section

Materials

Unless otherwise noted, carbon dioxide (99.999%), commercially available terminal alkynes, chloride compounds, Pluronic P123 (EO₂₀PO₇₀EO₂₀, MW = 5800), Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O), silver nitrate (AgNO₃) and other all reagents were used without further purification.

Synthesis of Catalysts

The mesoporous silica with cubic Ia3d symmetry (KIT-6) was prepared according to the published procedure^[51] using tri-block copolymer Pluronic P₁₂₃ (EO₂₀PO₇₀EO₂₀) as template by adding of n-butanol in an acidic aqueous solution.

M-CeO₂ was synthesized using KIT-6 as hard template and Ce(NO₃)₃·6H₂O as cerium source, followed by removal of KIT-6 using 2 M NaOH solution.^[22] In a typical synthesis, 4 g of Ce(NO₃)₃·6H₂O was dissolved in 20 ml of ethanol. This solution was incorporated into 1 g of KIT-6 by the incipient wetness impregnation technique. After the ethanol was evaporated at 60 °C, the composite was calcined at 400 °C to transfer the precursor into cerium oxide. The

bulk CeO₂ (B–CeO₂) was prepared as the above method without the addition of hard template.

Ag/M–CeO₂ catalyst was synthesized by the GBMR method. The specific synthesis process was as follows: an aqueous solution of AgNO₃ (10 mg/mL) was added dropwise to the mesoporous CeO₂ support under vigorous agitation for 10 min. The suspension was subjected to sonication (60 W, 40 kHz) at 25 °C for 3 h to mix the Ag precursor and M–CeO₂ evenly. The mixture solution was driven by a peristaltic pump (Baoding Lange Co., Ltd.) at a rotation speed of 200 rpm (~360 mL/min) to form a tubal cycling flow. A mixed solution of NaBH₄ and TRIS (1 mg/mL, 1 mL/min) was injected into the membrane reactor with two ceramic membrane tubes (φ = 3 mm × 160 mm, Hyflux Group of Companies, Singapore) by a constant flow pump (HLB-2020, Satellite Manufactory of Beijing). At the same time, H₂ was also flowed through the membrane reactor with the other two membrane tubes. The metal precursor solution flowed inside the glass tube reactor and outside the ceramic tubes. The mixed solution was infiltrated through the abundant holes (d = 40 nm) on the wall of the ceramic tubes into the glass tube reactor, where the reduction of metal ions occurred immediately when the two solutions met. The hydrogen bubbling-assisted stirring operation (40 mL/min) was developed to vigorously stir the solution and to make the reaction homogenous. The synthesis process was stopped until NaBH₄ solution was consumed completely. The reaction system was further vigorously bubbled with H₂ for 1 h and kept static for 1 h. Then, the product was filtered and washed with distilled water. The final products were dried in an oven at 60 °C overnight.

Characterization

The crystal structures of the samples were determined by a powder X-ray diffraction on a Shimadzu XRD 6000 using Ni-filtered Cu K α (λ = 0.15406 nm). The actual Ag content in the prepared catalysts was determined by ICP-OES using a Perkin–Elmer OPTIMA 7300 V. Specific surface area was measured by adsorption-desorption of N₂ gas at –196 °C with Micromeritics ASAP 2000 instrument. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas from the adsorption data. Before the measurements, the samples were outgassed at 120 °C for 10 h. The transmission electron microscopy (TEM) images were obtained with a JEM2100 electron microscope operated at 200 kV. The high-resolution transmission electron microscopy (HRTEM), the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM), and energy dispersive spectroscopy (EDS) for elemental mapping were carried out on a Tecnai F20 electron microscope. X-ray photoelectron spectra (XPS) were recorded on a Thermo Escalab-250XI spectrometer using Al K α ($h\nu$ = 1486.6 eV, 1 eV = 1.603 × 10^{–19} J) X-ray source. The binding energies were calibrated internally by the carbon deposit C 1s binding energy at 284.8 eV. Raman spectra were measured by Renishaw inVia Reflex Raman spectrometer under ambient conditions. The laser line at 532 nm was used as the exciting source. The temperature programmed desorption of CO₂ (CO₂-TPD) was carried out in a Micromeritics AutoChem II 2920. About 100 mg of the samples were pretreated with He (30 mL min^{–1}) at 400 °C for 30 min before being cooled to 50 °C. These samples were saturated with 10% CO₂/He blend for 120 min at 50 °C, and then purged with He for 60 min to remove physical adsorbed CO₂. TPD test was carried out from 50 °C to 700 °C with He at a heating rate of 10 °C min^{–1}. The desorbed CO₂ was continuously monitored by a thermal conductivity detector.

Computational Details

All the density functional theory (DFT) calculations were performed with the Vienna *ab initio* simulation package (VASP) code.^[52,53] The exchange and correlation energy functional was expressed in the GGA-PBE.^[54] Projector-augmented wave method^[55,56] was used to describe the interactions between ions and electrons. The valence electrons were solved in the plane-wave basis with a cutoff energy of 400 eV. The convergence criteria^[41] for the energy calculation and structure optimization were set to 1.0 × 10^{–5} eV and a force tolerance of 0.05 eV/Å, respectively. The Brillouin-zone integration^[57] was performed using a 1 × 1 × 1 Γ -centered k-point mesh with Gaussian smearing set to 0.05 eV. To accurately describe the localization of Ce 4f electrons, we conducted the DFT + U calculations with a value of U_{eff} = 4.5 eV. The setting of Hubbard-like term (U_{eff}) follows the approach explored by Fabris et al.,^[58] Cococcioni and De Gironcoli.^[59]

The adsorption energy is defined by Equation 1:

$$E_{\text{ads}} = E(\text{adsorbate/surface}) - E(\text{adsorbate}) - E(\text{surface}) \quad (1)$$

Where, $E(\text{adsorbate/surface})$ is the total energy of a surface interacting with adsorbate. $E(\text{adsorbate})$ and $E(\text{surface})$ are the energies of the isolated adsorbate and clean surface, respectively. Therefore, a negative value means exothermic adsorption. The more negative the adsorption energy, the stronger the adsorption.

The oxygen vacancy formation energy is calculated by Equation 2:

$$E_{\text{O}_v} = E_{\text{surface-O}_v} + \frac{1}{2} E_{\text{O}_2} - E_{\text{surface}} \quad (2)$$

Where E_{surface} is the energy of perfect surface; $E_{\text{surface-O}_v}$ is the energy of defective surface with an oxygen vacancy and E_{O_2} is the energy of a gas-phase O₂.

The charge density difference of CO₂ adsorption on catalyst surface is defined as $\Delta\rho = \rho_{\text{CO}_2/\text{substrate}} - \rho_{\text{CO}_2} - \rho_{\text{substrate}}$, where $\rho_{\text{CO}_2/\text{substrate}}$ is the charge density of the catalysts system with CO₂ adsorption; ρ_{CO_2} and $\rho_{\text{substrate}}$ are the charge densities of isolated CO₂ and catalysts, respectively.

General Procedure of Carboxylative Coupling Reaction

A 40 mL oven dried autoclave containing a stir bar was charged Ag/M–CeO₂ (120 mg), Cs₂CO₃ (2.0 mmol), alkyne (1.0 mmol), chloride compounds (1.5 mmol) and 5 mL dry DMF were added with syringe respectively after purging the autoclave with CO₂ three times. The sealed autoclave was pressurized to appropriate pressure with CO₂. The reaction mixture was stirred at 60 °C for 24 h, then the autoclave was cooled to room temperature and the remaining CO₂ was vented slowly. Then the reaction mixture was diluted with water (15 mL) and the solid residue was separated via centrifugation. Then the mixture was extracted with ethyl acetate (4 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried over Na₂SO₄ and filtered. The solvent was removed in vacuum, and the product was isolated by column chromatography on silica gel.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 21303264)

Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ • Carboxylative coupling • Ag nanoparticles • Mesoporous CeO₂ • Oxygen vacancies

- [1] a) C. Lastoskie, *Science*, **2010**, *330*, 595–596; b) P. Bhanja, A. Modak, A. Bhaumik, *ChemCatChem* **2018**, DOI: 10.1002/cctc.201801046.
- [2] G. L. Zhou, T. Wu, H. M. Xie, X. X. Zheng, *Int. J. Hydrogen Energy* **2013**, *38*, 10012–10018.
- [3] a) W. Wang, S. P. Wang, X. B. Ma, J. L. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703–3727; b) X. B. Lu, D. J. Darenbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462–1484; c) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1742; d) W. Z. Zhang, X. B. Lu, *Chin. J. Catal.* **2012**, *33*, 745; e) X. Zhang, Y. Z. Lv, X. L. Liu, G. J. Du, S. H. Yan, J. Liu, Z. Zhao, *RSC Adv.* **2016**, *6*, 76957–76963. f) Q. W. Song, Z. H. Zhou, L. N. He, *Green Chem.* **2017**, *19*, 3707–3728.
- [4] a) F. Manjolinho, M. Arndt, K. Gooßen, L. Gooßen, *ACS Catal.* **2012**, *2*, 2014–2021. b) E. Vessali, A. Hosseinian, M. Babazadeh, L. Edjlali, *Curr. Org. Chem.* **2018**, *22*, 315–322.
- [5] a) T. Tsujihara, K. Takenaka, K. Onitsuka, M. Hatanaka, H. Sasai, *J. Am. Chem. Soc.* **2009**, *131*, 3452–3453; b) M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43–81; c) L. Wang, J. Huang, S. Peng, H. Liu, X. Jiang, J. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1768–1772; *Angew. Chem.* **2013**, *125*, 1812–1816.
- [6] a) Y. Fukue, S. Oi, Y. Inoue, *Chem. Commun.* **1994**, *18*, 2091; b) W. Z. Zhang, W. J. Li, X. Zhang, H. Zhou, X. B. Lu, *Org. Lett.* **2010**, *12*, 4748–4751; c) K. Inamoto, N. Asano, K. Kobayashi, M. Yonemoto, Y. Kondo, *Org. Biomol. Chem.* **2012**, *10*, 1514–1516; d) J. N. Xie, B. Yu, Z. H. Zhou, H. Chen, N. Wang, L. N. He, *Tetrahedron Lett.* **2015**, *56*, 7059–7062; e) G. Xiong, B. Yu, J. Dong, Y. Shi, B. Zhao, L. N. He, *Chem. Commun.* **2017**, *53*, 6013–6016.
- [7] a) X. Zhang, W. Z. Zhang, L. L. Shi, C. Zhu, J. L. Jiang, X. B. Lu, *Tetrahedron* **2012**, *68*, 9085–9089; b) C. X. Guo, B. Yu, J. N. Xie, L. N. He, *Green Chem.* **2015**, *17*, 474–479; c) Z. Z. Zhang, R. J. Mi, F. J. Guo, J. Sun, M. D. Zhou, X. C. Fang, *J. Saudi Chem. Soc.* **2017**, *21*, 685–690; d) F. J. Guo, Z. Z. Zhang, J. Y. Wang, J. Sun, X. C. Fang, M. D. Zhou, *Tetrahedron* **2017**, *73*, 900–906.
- [8] B. Yu, J. N. Xie, C. L. Zhong, W. Li, L. N. He, *ACS Catal.* **2015**, *5*, 3940–3944.
- [9] A. A. Chaugule, A. H. Tamboli, H. Kim, *Chem. Eng. J.* **2017**, *326*, 1009–1019.
- [10] G. N. Bondarenko, E. G. Dvurechenskaya, E. S. Magomedov, I. P. Beletskaya, *Catal. Lett.* **2017**, *147*, 2570–2580.
- [11] G. Dutta, A. K. Jana, D. K. Singh, M. Eswaramoorthy, S. Natarajan, *Chem. Asian J.* **2018**, *10*, 1002–1009.
- [12] Z. P. Qu, F. L. Yu, X. D. Zhang, Y. Wang, J. S. Gao, *Chem. Eng. J.* **2013**, *229*, 522–532.
- [13] G. N. Li, L. Li, Y. Yuan, J. J. Shi, Y. Y. Yuan, Y. S. Li, W. R. Zhao, J. L. Shi, *Appl. Catal. B-Environ* **2014**, *158*, 341–347.
- [14] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.* **2016**, *116*, 5987–6041.
- [15] P. S. M. Kumar, S. Thiripuranthagan, T. Imai, G. Kumar, A. Pugazhendhi, S. R. Vijayan, R. Esparza, H. Abe, S. K. Krishnan, *ACS Sustainable Chem. Eng.* **2017**, *5*, 11290–11299.
- [16] H. B. Chong, P. Li, J. Xiang, F. Y. Fu, D. D. Zhang, X. R. Ran, M. Z. Zhu, *Nanoscale* **2013**, *5*, 7622–7628.
- [17] K. Y. Li, Y. Q. Zhao, C. S. Song, X. W. Guo, *Appl. Surf. Sci.* **2017**, *425*, 526–534.
- [18] J. J. Pang, X. T. Li, Z. H. Cao, J. J. Xu, X. Li, X. K. Zhang, *Appl. Surf. Sci.* **2018**, *439*, 420–429.
- [19] G. Z. Chen, Q. H. Xu, Y. Yang, C. C. Li, T. Z. Huang, G. X. Sun, S. X. Zhang, D. L. Ma, X. Li, *ACS Appl. Mater. Interfaces* **2015**, *7*, 23538–23544.
- [20] B. C. Liu, S. Y. Yu, Q. Wang, L. Liu, W. T. Hu, P. Jing, Y. Liu, W. J. Jia, Y. X. Liu, L. X. Liu, J. Zhang, *Chem. Commun.* **2013**, *49*, 3757–3759.
- [21] G. L. Zhou, H. R. Liu, K. K. Cui, H. M. Xie, Z. J. Jiao, G. Z. Zhang, K. Xiong, X. X. Zheng, *Int. J. Hydrogen Energy* **2017**, *42*, 16108–16117.
- [22] W. H. Shen, X. P. Dong, Y. F. Zhu, H. R. Chen, J. L. Shi, *Micropor. Mesopor. Mat.* **2005**, *85*, 157–162.
- [23] B. Naik, V. S. Prasad, N. N. Ghosh, *Powder Technol.* **2010**, *199*, 197–201.
- [24] M. Tan, Y. Choi, J. Kim, J. H. Kim, K. Fromm, *Polymer* **2018**, *10*, 1188.
- [25] Q. X. Zhou, S. L. Ma, S. H. Zhan, *Appl. Catal. B-Environ* **2018**, *224*, 27–37.
- [26] Y. G. Wang, F. Wang, Y. T. Chen, D. F. Zhang, B. Li, S. F. Kang, X. Li, L. F. Cui, *Appl. Catal. B-Environ* **2014**, *147*, 602–609.
- [27] F. Wang, S. He, H. Chen, B. Wang, L. Zheng, M. Wei, D. G. Evans, X. Duan, *J. Am. Chem. Soc.* **2016**, *138*, 6298–6305.
- [28] Q. Q. Tan, Z. S. Shi, D. F. Wu, *Ind. Eng. Chem. Res.* **2018**, *57*, 10148–10158.
- [29] C. Binet, M. Daturi, J. C. Lavalley, *Catal. Today* **1999**, *50*, 207–225.
- [30] Z. Hu, X. F. Liu, D. M. Meng, Y. Guo, Y. L. Guo, G. Z. Lu, *ACS Catal.* **2016**, *6*, 2265–2279.
- [31] C. Aliotta, L. F. Liotta, V. L. Parolab, A. Martorana, E. N. S. Muccillo, R. Muccillo, F. Deganello, *Appl. Catal. B-Environ* **2016**, *197*, 14–22.
- [32] L. Ma, C. Y. Seo, X. Y. Chen, J. H. Li, J. W. Schwanka, *Chem. Eng. J.* **2018**, *350*, 419–428.
- [33] S. J. Chang, M. Li, Q. Hua, L. J. Zhang, Y. S. Ma, B. J. Ye, W. X. Huang, *J. Catal.* **2012**, *293*, 195–204.
- [34] L. Ma, D. S. Wang, J. H. Li, B. Y. Bai, L. X. Fu, Y. D. Li, L. Ma, D. S. Wang, J. H. Li, *Appl. Catal. B-Environ* **2014**, *148*, 36–43.
- [35] Z. L. Wu, M. J. Li, J. Howe, H. M. Meyer, S. H. Overbury, *Langmuir* **2010**, *26*, 16595–16606.
- [36] G. M. Jiang, M. Wang, X. F. Gu, T. T. Chen, Y. F. Shang, Y. F. Tang, G. Q. Jiang, Y. J. Shi, *CrystEngComm* **2014**, *16*, 472–478.
- [37] S. J. Wu, Y. Yang, C. X. Lu, Y. Y. Ma, S. X. Yuan, G. R. Qian, *Eur. J. Inorg. Chem.* **2018**, 2944–2951.
- [38] L. Li, L. Song, H. D. Wang, C. Q. Chen, Y. S. She, Y. Y. Zhan, X. Y. Lin, Q. Zheng, *Int. J. Hydrogen Energy* **2011**, *36*, 8839–8849.
- [39] B. Liu, C. M. Li, G. Q. Zhang, X. S. Yao, S. Steven, C. Chuang, Z. Li, *ACS Catal.* **2018**, *8*, 10446–10456.
- [40] A. Trovarelli, J. Llorca, *ACS Catal.* **2017**, *7*, 4716–4735.
- [41] B. Liu, Z. Zhao, G. Henkelman, W. Y. Song, *J. Phys. Chem. C* **2016**, *120*, 5557–5564.
- [42] B. Liu, J. Liu, T. Li, Z. Zhao, X. Q. Gong, Y. Chen, A. J. Duan, G. Y. Jiang, Y. C. Wie, *J. Phys. Chem. C* **2015**, *119*, 12923–12934.
- [43] S. Kattel, P. Liu, J. G. G. Chen, *J. Am. Chem. Soc.* **2017**, *139*, 9739–9754.
- [44] S. Kattel, B. H. Yan, J. G. G. Chen, P. Liu, *J. Catal.* **2016**, *343*, 115–126.
- [45] Y. Guo, S. Mei, K. Yuan, D. J. Wang, H. C. Liu, C. H. Yan, Y. W. Zhang, *ACS Catal.* **2018**, *8*, 6203–6215.
- [46] X. H. Liu, J. G. Ma, Z. Niu, G. M. Yang, P. Cheng, *Angew. Chem.* **2015**, *54*, 988–991.
- [47] a) D. Y. Yu, M. X. Tan, Y. G. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 969–974. b) Z. L. Wu, Q. G. Liu, X. F. Yang, X. Ye, H. M. Duan, J. Zhang, B. Zhao, Y. Q. Huang, *ACS Sustainable Chem. Eng.* **2017**, *5*, 9634–9639; c) X. W. Lan, C. Du, L. L. Cao, T. T. She, Y. M. Li, G. Y. Bai, *ACS Appl. Mater. Interfaces* **2018**, *10*, 38953–38962.
- [48] Z. L. Wu, L. Sun, Q. G. Liu, X. F. Yang, X. Ye, Y. C. Hu, Y. Q. Huang, *Green Chem.* **2017**, *19*, 2080–2085.
- [49] a) R. A. Molla, K. Ghosh, B. Banerjee, M. A. Iqbal, S. K. Kundu, S. M. Islam, A. Bhaumik, *J. Colloid Interface Sci.* **2016**, *477*, 220–229; b) M. Trivedi, Bhaumik, A. Kumar, G. Singh, A. Kumar, N. P. Rath, *New J. Chem.* **2016**, *40*, 3109–3118; c) N. N. Zhu, X. H. Liu, T. Li, J. G. Ma, P. Cheng, G. M. Yang, *Inorg. Chem.* **2017**, *56*, 3414–3420.
- [50] a) S. Das, P. Mondal, S. Ghosh, B. Satpati, S. Deka, S. K. M. Islam, T. Bala, *New J. Chem.* **2018**, *42*, 7314–7325; b) A. H. Chowdhury, S. Ghosh, S. K. M. Islam, *New J. Chem.* **2018**, *42*, 14194–14202.
- [51] T. W. Kim, F. Kleitz, B. Paul, R. Ryoo, *J. Am. Chem. Soc.* **2005**, *127*, 7601–7610.
- [52] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.
- [53] G. Kresse, J. Furthmüller, *Comp. Mater. Sci.* **1996**, *6*, 15–50.
- [54] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [55] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.
- [56] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758–1775.
- [57] H. Monkhorst, J. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.
- [58] S. Fabris, S. D. Gironcoli, S. Baroni, G. Vicario, G. Balducci, *Phys. Rev. B* **2005**, *72*, 237102.
- [59] M. Cococcioni, S. D. Gironcoli, *Phys. Rev. B* **2005**, *71*, 035105.

Manuscript received: January 7, 2019

Revised manuscript received: February 25, 2019

Version of record online: April 3, 2019