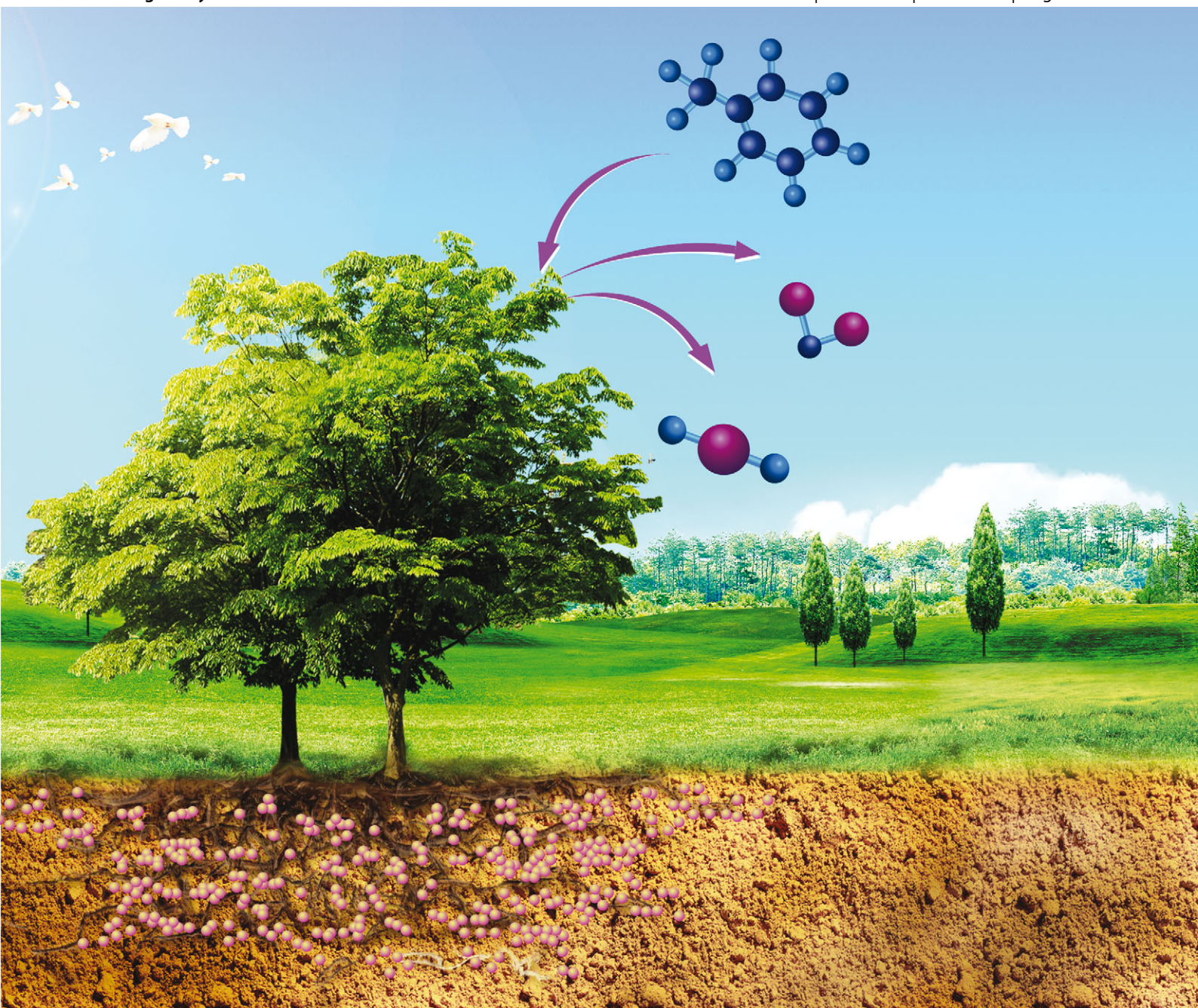


Catalysis Science & Technology

www.rsc.org/catalysis

Volume 3 | Number 6 | June 2013 | Pages 1425–1648



ISSN 2044-4753

RSC Publishing

COVER ARTICLE

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High thermal stability of ceria-based mixed oxide catalysts supported on ZrO₂ for toluene combustion



2044-4753(2013)3:6;1-7

High thermal stability of ceria-based mixed oxide catalysts supported on ZrO₂ for toluene combustion†

Cite this: *Catal. Sci. Technol.*, 2013, **3**, 1480

Received 6th November 2012,
Accepted 15th January 2013

DOI: 10.1039/c3cy20754d

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Cu–Mn–Ce mixed oxide catalysts (CMCs) supported on ZrO₂ were prepared by an impregnation method. Their catalytic activity was evaluated by a model reaction, that of toluene combustion. 5% CMC/ZrO₂ catalysts show a very high activity and thermal stability, and 90% of toluene conversion could be obtained at temperatures below 260 °C, even with the catalyst being annealed at 900 °C. A new phase of Zr_{0.88}Ce_{0.12}O₂ in the interface was formed by the interaction between ZrO₂ and CMC on the catalyst with low loading. Zr_{0.88}Ce_{0.12}O₂ serves as the actual carrier of the active phase, and can significantly improve the thermal stability of the catalyst.

1. Introduction

Volatile organic compounds (VOCs), emitted from many industrial processes and transportation activities, are one of the major contributors to air pollution. They are also known to have adverse effects on human health. Catalytic combustion can efficiently eliminate dilute volatile organic pollutants at relatively low temperatures (200–500 °C) and with lower energy consumption compared with direct incineration.^{1–2} Noble metal catalysts have been widely used in catalytic combustion of VOCs.^{3–7} However, in addition to the high cost, noble metal catalysts are susceptible to poisons, such as the impurities in the feed stream or the intermediates formed during oxidation. Thus, intense efforts are being directed towards the design and synthesis of metal oxide-based catalytic materials as a substitute for noble metal catalysts.^{8–12}

Cerium dioxide (CeO₂) doped with specific metal ions (such as Cu, Mn and Co *etc.*) with the formation of a ceria-based solid solution structure is a very promising catalytic material in a catalytic combustion reaction because of its high catalytic activity.^{13–19} However, active structures of CeO₂-based mixed

oxides mainly depend on lattice defects and ion vacancies, which are formed by metal ion doping. These defects and vacancies provide major transport channels for surface oxygen (O₂[–], O[–]), lattice oxygen (O^{2–}) and high catalytic activity at low temperatures.^{11,19} On the other hand, these defects and vacancies also function as channels for diffusion sintering, *i.e.*, in these channels, metal ions readily migrate and change in valence, which results in a decrease in surface areas and activities at high temperatures. For this reason, it is usually difficult for CeO₂-based oxide catalysts to achieve high catalytic activity and high thermal stability at the same time.^{20,21} It has become the bottleneck for the wide application of these types of catalysts.

For the latter research has shown that, the incorporation of structural additives (Al, Zr, La and Y) into the CeO₂ lattice is usually an effective way to isolate active nanoparticles, and delay sintering at high temperatures.^{20,22–26} But a large number of additive doping would result in damaging the original active phase of CeO₂-based mixed oxides. In the present work, we report a type of mixed ceria-based oxide catalysts (consisting of Cu, Mn and Ce, Cu/Mn/Ce = 1/2/4 (mol), and abbreviated as CMC) with high activity and thermal stability, which can be prepared by simple impregnation of appropriate amounts of the above mixed oxides (CMC) on ZrO₂. The structural features and redox properties of catalysts were also investigated.

2. Experimental

2.1 Catalyst preparation

Hydrous zirconia was prepared by dropwise addition of a solution of ZrOCl₂ (0.15 M) into a well-stirred ammonium solution (5.0%) at room temperature. The pH during precipitation was carefully controlled at and maintained 10. The precipitate formed, as described above, was collected by filtering and washing with deionized water until there was no detectable Cl[–], dried at 110 °C and calcined at 500 °C to produce a ZrO₂ support with a BET surface area of 65 m² g^{–1}. Samples of CMC/ZrO₂ were prepared by loading the support with an appropriate amount of CuO, MnO and CeO₂ by an impregnation method with Cu, Mn

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cy20754d

and Ce nitrate precursors (the molar ratio of Cu/Mn/Ce is 1/2/4), the concentration of which was adjusted to yield catalysts containing 2.5, 5, 10, 20 and 40 wt% Cu–Mn–Ce–O (the load calculated by the weight of CuO, MnO and CeO₂). The catalysts were dried at 110 °C and calcined at different temperatures, which were 500, 800, 900 and 1000 °C for 3 h in flowing air.

2.2 Catalyst characterization

The specific surface area of catalysts was measured by the BET method from the nitrogen adsorption isotherms obtained at 77 K on samples degassed at 427 K with a micromeritics ASAP 2020 instrument.

The XRD data of the samples was collected on a SCINTAG XTRA X-ray diffractometer equipped with Ni filtered Cu ka ($\lambda = 1.542 \text{ \AA}$, 40 kV) radiation. The data were collected in the 2θ range of 10–60° with a step size of 0.033°.

The TPR experiments were performed using a Fine-Tech Autochem 3010E instrument. A weighed amount of the samples (200 mg) was placed in a quartz reactor, pretreated in a flow of Ar gas at 250 °C for 2 h, and cooled to 70 °C. A gas mixture of H₂ (5%)–Ar (95%) was then passed (30 ml min⁻¹) through the reactor. The temperature rose to 750 °C at a heating rate of 10 K min⁻¹. A TCD detector was employed at the outlet of the reactor to measure the volume of hydrogen consumed during reduction of the samples.

2.3 Catalytic activity measurement

Catalytic combustion of toluene was conducted in a fixed-bed quartz tube reactor (i.d. 8 mm) at atmospheric pressure. 500 mg of catalyst was packed at the bed of the reactor. The reaction feed (0.5 vol% toluene in air) was introduced to the catalyst at a flow rate of 200 mL min⁻¹ (gas hourly space velocity (GHSV) = 24 000 mL h⁻¹ (geat.)⁻¹). The reactor effluent was analyzed online at a given temperature by HP 6890 gas chromatography equipped with an FID detector.

3. Results and discussion

3.1 Activity test

Fig. 1 shows the light-off curves of toluene combustion over CMC/ZrO₂ with different CMC loadings. As seen in Fig. 1(a), the activity is enhanced significantly upon the loading of CMC with catalysts calcined at 500 °C. However, with an increase in calcination temperature to 900 °C, the activities of high CMC loading catalysts (10–40%) decrease rapidly. Unexpectedly, 5% CMC/ZrO₂ shows a surprising performance, including thermal stability and activity. As illustrated in Fig. 1(b), toluene can be totally converted at 260 °C, over 5% CMC/ZrO₂, after calcination at 900 °C that is comparable to those of conventional noble metal catalysts, such as Pd and Pt.^{3,7} Moreover, following calcination at 900 °C, the combustion rate of toluene is enhanced for the 5% CMC/ZrO₂ catalyst. The effect of the ageing time at 800 °C on the activity of 5% CMC/ZrO₂ was also investigated (see Fig. 2). It was found that its T₉₀ remains almost unchanged after 15 h. However, serious deactivation was found when the catalyst was calcined at a temperature of 1000 °C.

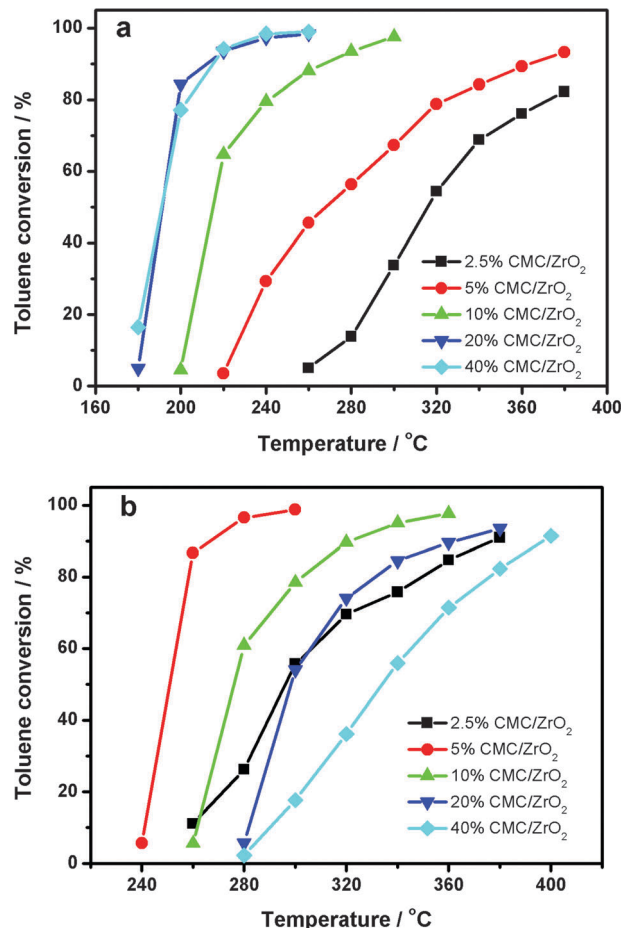


Fig. 1 Light-off curves of toluene combustion over CMC/ZrO₂ catalysts with different CMC loadings, (a) catalysts calcined at 500 °C, (b) catalysts calcined at 900 °C.

Long-term stability is one of the most important properties of a catalyst. A time-on-stream experiment for the 5% CMC/ZrO₂ catalyst calcined at 800 °C was carried out to demonstrate

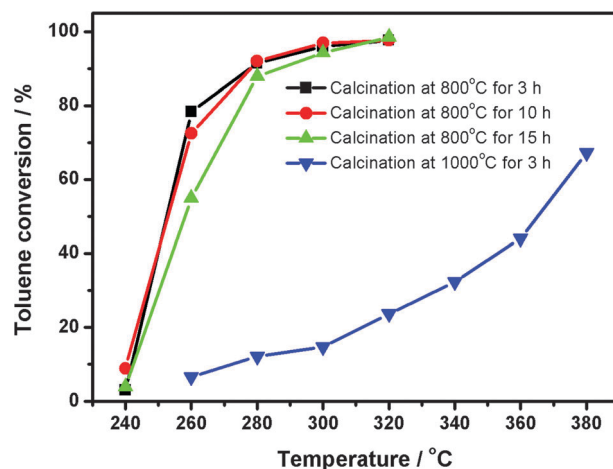


Fig. 2 The effect of calcination time and temperature on the activity of 5% CMC/ZrO₂ catalysts.

the stability of the catalytic activity, and the results are shown in Fig. 3. During the experiment, the reaction temperature increases from 260 to 300 °C and then 500 °C for 6 h, and then the reaction temperature decreases back to 260 °C for activity comparison. The catalyst shows no noticeable deactivation after the experiment (about 33 h), indicating a good repeatability and stability in the VOC stream.

3.2 XRD characterizations

In order to achieve a deep insight into the structure evolution in thermal treatment, X-ray powder diffraction experiments of the catalysts were carried out. Fig. 4 presents the XRD patterns of 5% and 40% CMC/ZrO₂ calcined at different temperatures. In the XRD patterns of 5% CMC/ZrO₂ calcined at 500 °C, some major diffraction peaks at $2\theta = 28.34^\circ$, 31.48° , which are attributed to a monoclinic ZrO₂ structure (JCPDS 80-0966) are identified, indicating that CMC is uniformly dispersed on ZrO₂. However, upon further treatment at 900 °C, a new weak peak at $2\theta = 30.0^\circ$ is observed for 5% CMC/ZrO₂, which is attributed to the tetragonal Zr_{0.88}Ce_{0.12}O₂ solid solution structure (JSPDS 82-1398). However, with further increase in calcination temperature to 1000 °C, the diffraction peak of Zr_{0.88}Ce_{0.12}O₂ disappears and another weak peak at $2\theta = 28.54^\circ$, which is attributed to a cubic CeO₂ fluorite structure (JCPDS 34-0394) evolves. After calcination at 1000 °C, the catalytic activity also declines significantly (see Fig. 2).

The XRD pattern of 40% CMC/ZrO₂ catalyst calcined at 500 °C reveals a broad reflection at 2θ between 28.0° and 29.0° due to the overlapping diffraction of monoclinic ZrO₂ and cubic CeO₂. These two peaks are separated when the catalyst is further calcined at 900 °C. Zr_{0.88}Ce_{0.12}O₂ is not observed from the samples, which were calcined at 900 °C. There are no Cu and Mn oxide phases presented in the XRD patterns of the catalysts, which indicated that a ceria-based solid solution structure is formed by doping of Cu and Mn ions. It is confirmed by comparing the XRD patterns of pure CeO₂ and CMC catalysts (ESI,† Fig. S1) that there is a decrease of the lattice parameter of the CMC catalysts, indicating that ceria-based solid solutions are formed by partial replacement of

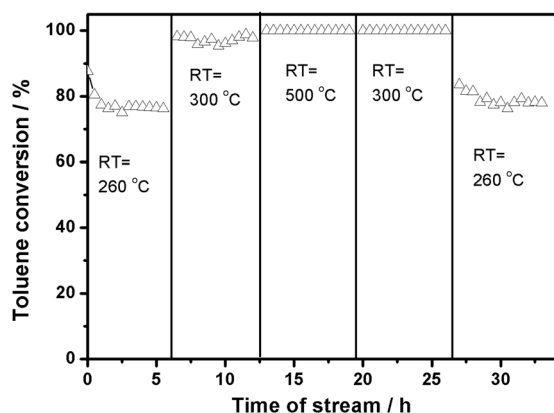


Fig. 3 Catalytic combustion of toluene over the 5% CMC/ZrO₂ catalyst calcined at 800 °C.

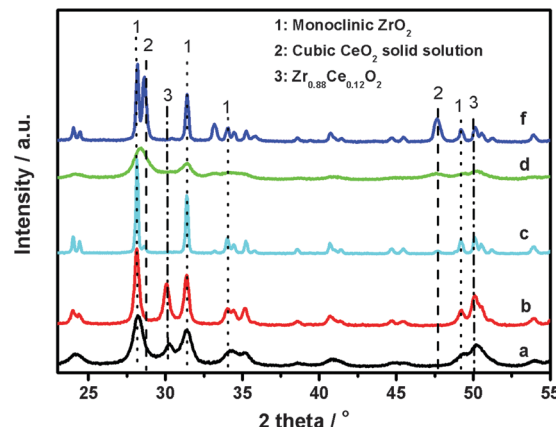


Fig. 4 XRD patterns of CMC/ZrO₂ catalysts calcined at 500 and 900 °C with different CMC loadings. (a) 5% CMC/ZrO₂-500; (b) 5% CMC/ZrO₂-900; (c) 5% CMC/ZrO₂-1000; (d) 40% CMC/ZrO₂-500; (f) 5% CMC/ZrO₂-900.

Ce⁴⁺ with these smaller transition metal cations (Cu²⁺ and Mn³⁺). However, the solubility limitation of Cu and Mn cations in CeO₂ reported by Aranda²⁷ and Kang²⁸ is less than 10 mol%, and is highly dependant on the preparation procedure. We suggest that the excess Cu and Mn in CMC catalysts is highly dispersed on the surface of CeO₂ as CuO_x, MnO_x or their mixed oxides. The HRTEM image of 40% CMC/ZrO₂-500 catalyst (see ESI,† Fig. S2) clearly shows several lattice fringes of the crystallinity of Cu and Mn oxides beside CeO₂ and ZrO₂. Therefore, it is reasonable to attribute the high activity of the CMC catalyst to double active structures. One has a mixed structure of Cu and Mn oxides with the function of activation of organic molecule. The other one has a ceria-based solid solution structure with the function of transportation of active oxygen, including surface and lattice oxygen.

We suggest that a sharp decrease in activity of 5% CMC/ZrO₂ is accompanied by the disappearance of Zr_{0.88}Ce_{0.12}O₂, demonstrating that the existence of Zr_{0.88}Ce_{0.12}O₂ in the interface is the key factor in stabilizing the active phase of the CMCs at high temperatures. However, excessive amounts of the CMC over the surface of ZrO₂ do not necessarily lead to the formation of Zr_{0.88}Ce_{0.12}O₂. Higher loading of CMC is more likely to sinter and results in the separation of Ce⁴⁺ and Zr⁴⁺ in the interface, and finally the disappearance of Zr_{0.88}Ce_{0.12}O₂.

3.3 H₂-TPR characterizations

The reducibility of 5% and 40% CMC/ZrO₂ was also investigated by H₂-TPR measurements (demonstrated in Fig. 5). It is an unexpected phenomenon that the initial reduction temperature of 5% CMC/ZrO₂ decreases with calcination temperature, indicating the improvement in the mobility of surface and lattice oxygen after calcination at 900 °C. This result is not consistent with the common understanding that it is more difficult to reduce metal oxides after calcination at high temperatures due to the decrease in surface area.^{13,17} According to the XRD results, it is suggested that a decrease in reduction temperature is probably closely related to the formation of a new Zr_{0.88}Ce_{0.12}O₂ phase. Under thermal treatment conditions,

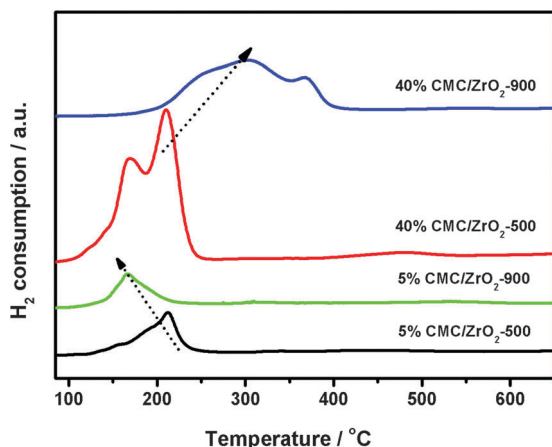


Fig. 5 H_2 -TPR profiles of CMC/ ZrO_2 catalysts calcined at 500 and 900 °C with different CMC loadings.

the Ce^{4+} of the CeO_2 -based solid solution would enter into the ZrO_2 support lattice, which may then result in the formation of some new lattice defects and increase of oxygen vacancies. On the contrary, the H_2 -reduction process of 40% CMC/ ZrO_2 is similar to traditional metal oxide catalysts. Due to the sintering of surface CMCs, the reduction peaks at a temperature of around 160 °C become smaller with an increase in calcination temperature.

By combining TPR profiles with the activities of catalysts, we propose that the H_2 -consumption of reduction within a temperature range of 150–200 °C directly relates to the activity of the corresponding catalyst. Namely, the active surface oxygen, which is reduced at low temperatures, is the key factor responsible for activity in catalytic combustion. In addition, the reduction degree (χ) of the catalysts is also listed in Table 1. The catalysts with lower loadings have higher degrees of reduction, indicating that utilization of surface active oxygen would be enhanced by a dispersion effect by the ZrO_2 support.

The evolution of the structure of CMC/ ZrO_2 with low loading during calcination at different temperatures is proposed. Firstly, Cu, Mn and Ce nitrates over ZrO_2 decompose and form a highly dispersed phase of metal oxide nanoparticles at low temperatures (≤ 500 °C). The active structure of CeO_2 -based

solid solution and Cu–Mn mixed oxides are gradually formed at temperatures above 500 °C. As the calcination temperature continues to rise, the interaction between ZrO_2 and CeO_2 becomes stronger, which finally leads to the formation of a new phase, $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$, in the interface. The HRTEM image of the 5% CMC/ ZrO_2 -900 sample (ESI,† Fig. S3) shows that the crystal plane of ZrO_2 changes because Ce^{4+} is inserted into the lattice of ZrO_2 under the thermal effect. Then, the formed $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$ would serve as the actual carrier of the active phase of CMC. $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$ has higher thermal stability than other active phases. As a result, the catalyst is able to maintain its active structure even when aged at 900 °C. Meanwhile, $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$ can further create new lattice defects and promote the mobility of active oxygen. At temperatures higher than 900 °C, the sintering of ZrO_2 and CeO_2 is inevitable because at these temperatures Zr^{4+} and Ce^{4+} in $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$ migrate to the sintered particles of ZrO_2 and CeO_2 , respectively, which then results in the disappearance of $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$. The $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$ solid solution tends to form at CMC/ ZrO_2 with a low CMC loading, which can be attributed to the high mobility of Ce^{4+} for highly dispersed small particles of CeO_2 with a high surface free energy. However, for catalysts with high CMC loadings, the sintering of CMC is more likely to take place because of the weak interaction between ZrO_2 and large particles of CeO_2 .

4. Conclusions

Highly active CeO_2 -based oxides as a substitute for expensive noble metal catalysts are being developed to apply to many catalytic oxidation reactions, such as soot combustion, TWC and CO oxidation. Unfortunately, their poor thermal stability limits their wider application in industry. Loading mixed CeO_2 -based oxides on ZrO_2 is a simple and effective method to improve the thermal stability of catalysts. Especially during the exothermic oxidation reactions, the ZrO_2 carrier can not only stabilize the surface active structure of CeO_2 -based oxides by formation of a $\text{Zr}_{0.88}\text{Ce}_{0.12}\text{O}_2$ solid solution in the interface, but can also enhance the mobility of active oxygen and improve the catalytic performance of total oxidation.

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Table 1 Surface area, hydrogen consumption (TPR) and reduction degree over CMC/ ZrO_2 catalysts

Samples	BET ($\text{m}^2 \text{g}^{-1}$)	Reduction temperature ^a (°C)	H_2 consumption ^b (mmol g^{-1})	Reduction degree (χ) CMC- $\text{O}_{2-\chi}$
5% CMC/ ZrO_2 -500	52.3	215	0.217	0.647
5% CMC/ ZrO_2 -900	11.5	165	0.165	0.492
40% CMC/ ZrO_2 -500	47.2	165	1.027	0.510
40% CMC/ ZrO_2 -900	0.46	300	0.783	0.389

^a Temperature at the first reduction peak. ^b Take CuO powder as the standard sample for calculating H_2 consumption.

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