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# $Ce_{0.5}Zr_{0.5}O_2$修饰的 Ni/SiC、Fe/SiC 和 Co/SiC 催化燃烧甲烷性能

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# Methane Catalytic Combustion over Ni/SiC, Fe/SiC and Co/SiC Modified by $Zr_{0.5}Ce_{0.5}O_2$ Solid Solution

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## 1 ICP-MS Characterization

**Table S1 Metal loadings (*w*) of different fresh and used catalysts**

| Sample | $w_{Zr}$/% | | $w_{Ce}$/% | | $w_{Ni}$/% | | $w_{Fe}$/% | | $w_{Co}$/% | |
|---|---|---|---|---|---|---|---|---|---|---|
| | fresh | uesd | fresh | uesd | fresh | uesd | fresh | uesd | fresh | uesd |
| Ni/$Ce_{0.5}Zr_{0.5}O_2$/SiC | 2.48 | 2.32 | 2.42 | 2.31 | 14.78 | 13.60 | | | | |
| Fe/$Ce_{0.5}Zr_{0.5}O_2$/SiC | 2.45 | 2.37 | 2.39 | 2.32 | | | 14.56 | 13.64 | | |
| Co/$Ce_{0.5}Zr_{0.5}O_2$/SiC | 2.41 | 2.35 | 2.43 | 2.36 | | | | | 14.74 | 14.02 |

The metal loadings of different catalysts measured by ICP-MS are listed in Table S1. In the fresh catalysts, the contents of Zr and Ce are around 2.5% (*w*), indicating the formation of $Ce_{0.5}Zr_{0.5}O_2$ solid solution. The loading amounts of Ni, Fe and Co in fresh catalysts are 14.78%, 14.56%, and 14.74% (*w*), respectively, and decrease slightly after reaction, indicating that high surface area SiC can stabilize the active phases.

## 2 HRTEM Characterization

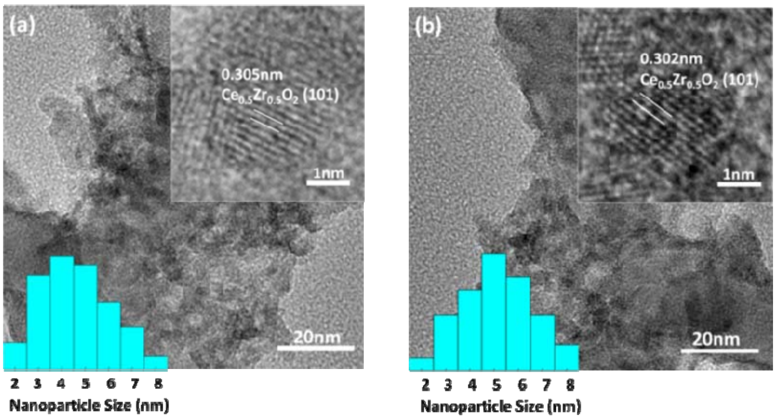

**Fig.S1 HRTEM images of fresh (a) and used (b) $Ce_{0.5}Zr_{0.5}O_2$/SiC catalyst; and the size distribution of nanoparticles**

The insert pictures are HRTEM images of $Ce_{0.5}Zr_{0.5}O_2$ nanoparticles before (a) and after reaction (b).

Fig.S1 shows HRTEM images of fresh and used $Ce_{0.5}Zr_{0.5}O_2$/SiC catalysts. The lattice spacing of 0.305 nm is ascribed to the (101) plane of $Ce_{0.5}Zr_{0.5}O_2$. The $Ce_{0.5}Zr_{0.5}O_2$ nanoparticles are well dispersed on the SiC substrate with an average size of 4.6 nm. The particle size only has a slight increase from 4.6 to 5.2 nm after cyclic reaction, suggesting that $Ce_{0.5}Zr_{0.5}O_2$/SiC has a good thermal stability.

## 3 XRD Characterization

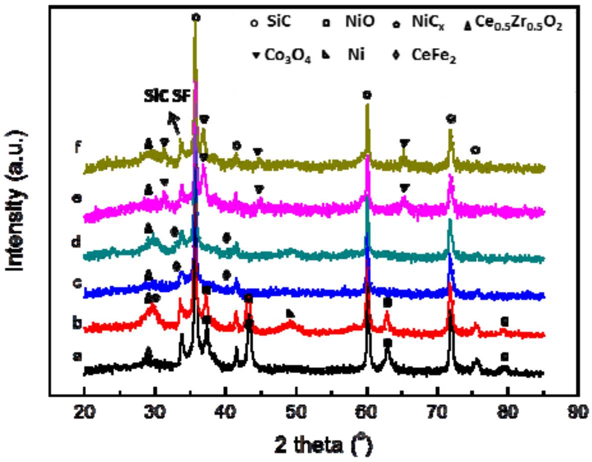

**Fig.S2 XRD patterns of fresh (a, c, e) and used (b, d, f) Ni/$Ce_{0.5}Zr_{0.5}O_2$/SiC (a, b), Fe/$Ce_{0.5}Zr_{0.5}O_2$/SiC (c, d) and Co/$Ce_{0.5}Zr_{0.5}O_2$/SiC (e, f) catalysts**

Fig.S2 shows the XRD patterns of three fresh and used catalysts. The strong diffraction peak ($2\theta$=35.8°) can be indexed to $\beta$-SiC. The peak at 29.3° assigning to $Ce_{0.5}Zr_{0.5}O_2$ is broad, indicating that the grain size of $Ce_{0.5}Zr_{0.5}O_2$ is small. The intensity of all the $Ce_{0.5}Zr_{0.5}O_2$ peaks significantly increases after reaction. Moreover, the $Ce_{0.5}Zr_{0.5}O_2$ peaks shift to higher $2\theta$ degree, indicating that some Ni, Fe and Co atoms have been inserted into $Ce_{0.5}Zr_{0.5}O_2$ lattice in the reaction process, forming a new solid solution containing active component. Ni exists in the form of NiO in the fresh Ni/$Ce_{0.5}Zr_{0.5}O_2$/SiC catalyst. However, partial NiO is reduced to metallic Ni and some $NiC_x$ is formed in the used catalyst (Fig.S2(b)), indicating that a certain amount of carbon has been deposited on Ni active component. Only $CeFe_2$ alloy is detected in both fresh and used Fe/$Ce_{0.5}Zr_{0.5}O_2$/SiC catalysts, suggesting that Fe solid solution is formed during the preparation process. As for Co/$Ce_{0.5}Zr_{0.5}O_2$/SiC catalyst, Co exists in the form of $Co_3O_4$ both in fresh and used ones.

## 4 XPS Characterization

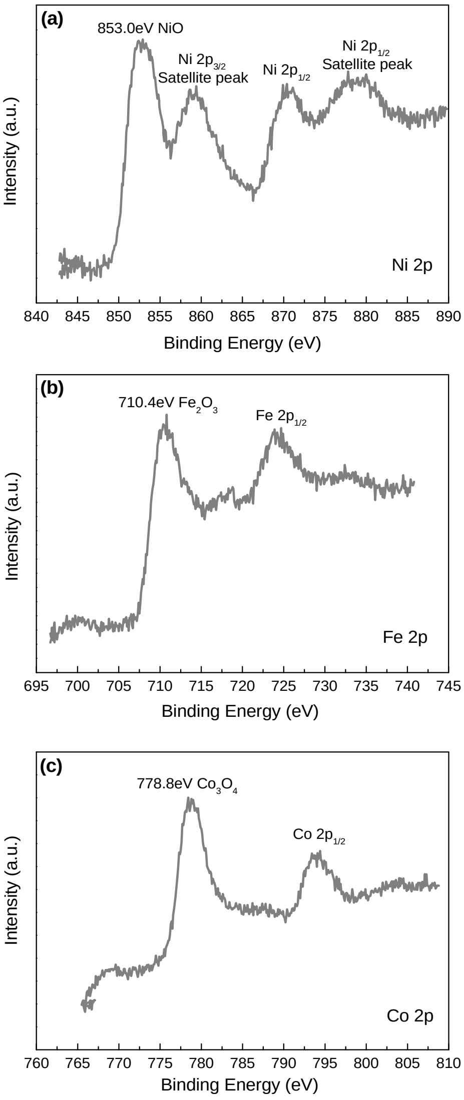

**Fig.S3 XPS spectra of fresh Ni/$Ce_{0.5}Zr_{0.5}O_2$/SiC, Fe/$Ce_{0.5}Zr_{0.5}O_2$/SiC, and Co/$Ce_{0.5}Zr_{0.5}O_2$/SiC**

(a) Ni 2*p*, (b) Fe 2*p*, (c) Co 2*p*

Fig.S3 shows the XPS spectra of the three fresh catalysts. It can be seen that the $2p_{3/2}$ binding energy (BE) values of NiO, $Fe_2O_3$ and $Co_3O_4$ are 853.0, 710.4, and 778.8 eV,[1,2] which show negative shift compared with theoretical values of 853.8, 711.3, and 779.5 eV. This suggested that electron cloud density around transition metal atoms increases due to the abundant oxygen vacancy and excellent oxygen transfer ability of $Ce_{0.5}Zr_{0.5}O_2$ solid solution. The increase of electron cloud density weakens the M-O bonds and enhances the reduction ability of NiO, $Fe_2O_3$, and $Co_3O_4$. As a result, the absorption, dissociation and activation of oxygen and $CH_4$ are significantly improved. Moreover, the insertion of partial Ni, Fe, and Co into $CeO_2$ lattice generate more crystal defects and oxygen vacancies and further increase the electron cloud density around transition metal atoms. Therefore the gradually weakening of M-O bonds results in the increasing activity of catalysts.

## References

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