

Co₃O₄ with different morphologies for catalytic combustion of CO and CH₄ and investigation the role of their diverse oxygen species with oxygen isotopic exchange reaction

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Introduction

The compositions, intrinsic crystal structures, morphologies and microstructures of materials have great inference on its for physicochemical properties. In this present work, five different morphology of Co₃O₄ have been obtained, namely nanoslice(NS), nanoparticle(NP), nanoflower(NF), nanonest(NN) and nanopolyhedron(NPL).

Further, investigation was carried out to study the oxygen mobility using oxygen isotopic exchange reaction (OIE). The result obtained provided an insight about the oxidation mechanism over these materials and elucidate the role of surface and bulk oxygen, observed to be different in the samples. To the best of our knowledge, there is dirt information about the involvement of OIE to explain catalytic activity with various morphologies for the catalytic combustion of CO and CH₄.

Materials and Methods

The catalysts were prepared using hydrothermal method and calcinating method. CO and CH₄ oxidation reaction was performed in a tubular microreactor. 200 mg of material was inserted inside the reactor. The reaction flow composed of composed of 2 vol.% of CO or CH₄-20 vol.% O₂-bal, and balanced by Ar with a total flow rate of 100 ml min⁻¹ (corresponding to a space velocity of approximately 35,000 h⁻¹). The reactor was regulated continuously using a temperature controller with a thermocouple inserted into the catalyst bed. The mixed gases were monitored using gas chromatography (GC4000A) equipped with a thermal conductivity detector (TCD).

Results and Discussion

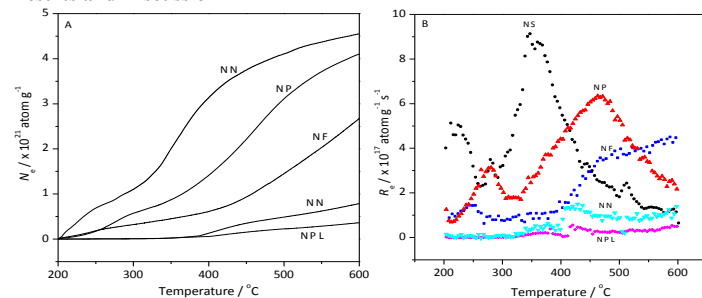


Fig. 1 Evolution of the number of exchanged oxygen atoms (N_e) and the exchange rate (R_e) versus temperature of reaction over Co₃O₄

For NS, NP and NF, two steps (low temperature and high temperature) were observed in Fig.1A. These two steps can be ascribed to the surface and bulk oxygen activation[1,2]. Because of low exchange for NN and NPL samples, only one step occurring at high temperature was seen. For the inverse relationship between R_e^{\max} and oxygen mobility (lower the R_e^{\max} temperature, higher will be the oxygen mobility) [1,2], it is clear that NS has the best exaltation of the bulk oxygen mobility in the materials (lowest temperature at R_e), while the NPL is worst. Under normal circumstances, the low temperature redox performance can bring good low-temperature oxygen transfer ability. This can be a very good match with the TPR. Other samples also conform to this rule.

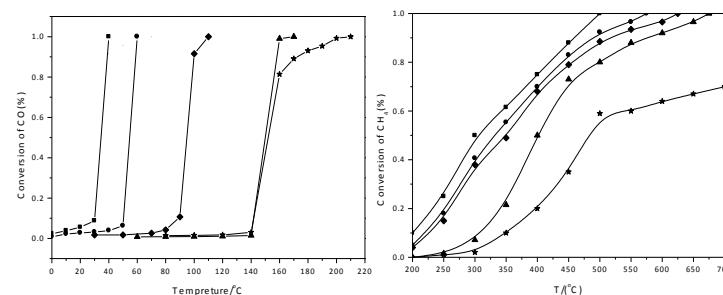


Figure 2. CO and CH₄ conversion versus reaction temperature for ■:nanoslice, ●:nanoparticle, ◆:nanoflower, ▲:nanonest, ★:nanopolyhedron

In the catalytic activity test, CO and CH₄ combustion showed similar behavior, NS sample had best activity for the two systems and matched well with the result of OIE results. The activity results can also match well with the surface areas and redox abilities of these Co₃O₄ samples.

Significance

For the possible substitutes for noble metals and excellent properties in this area of catalysis and lithium-ion batteries, the research of synthesizing different morphology micro/nano-Co₃O₄ has attracted extensive study[3,4]. Five different morphology of Co₃O₄ have been obtained. Oxygen isotopic exchange reaction (OIE) was innovatively applied in this reaction and well explain the relationship of catalytic activity and oxygen species, which can have good guiding significance in the field of morphologies.

References

- Yang, W.; Zhang, R.; Chen, B.; Bion, N.; Duprez, D., J. Catal. 295(2012) 45-58.
- Yang, W.; Zhang, R.; Chen, B.; Bion, N.; Duprez, D.; Hou, L.; Zhang, H.; Royer, S., Chem. Commun. 49(2013) 4923.
- Chen, J. S.; Zhu, T.; Hu, Q. H.; Gao, J.; Su, F.; Qiao, S. Z.; Lou, X. W., ACS Appl Mater Interfaces 2(2010) 3628-35.
- Xu, R.; Wang, J.; Li, Q.; Sun, G.; Wang, E.; Li, S.; Gu, J.; Ju, M., J. Solid State Chem. 182(2009)3177-3182.