



A facile approach for the preparation of biomorphic CuO–ZrO₂ catalyst for catalytic combustion of methane

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ABSTRACT

A series of novel biomorphic CuO–ZrO₂ catalysts were prepared using a cotton bio-template and compared with conventional CuO–ZrO₂ catalysts. The physical and chemical properties of the as-obtained catalysts were characterized by techniques including X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), H₂-temperature programmed reduction (H₂-TPR), and O₂-temperature programmed desorption (O₂-TPD). The catalytic combustion of methane was chosen as the probe reaction. The results suggested that the bio-template method prepared porous biomorphic CuO–ZrO₂ catalysts consist of hollow microtubes. Comparing with conventional CuO–ZrO₂ catalysts, biomorphic CuO–ZrO₂ catalysts displayed better reducibility and oxygen mobility, stronger metal-oxides synergistic effect, appropriate particle size distribution, and lower activation energy. The crystalline state of zirconia transformed from a single crystallite phase of t-ZrO₂ into a complex of m-ZrO₂ and t-ZrO₂ after introducing the bio-template. With proper CuO content (20 mol%), the biomorphic CuO–ZrO₂ catalyst displayed preponderant properties. The compensation of surface lattice oxygen from bulk lattice oxygen was more available at high reaction temperatures.

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1. Introduction

Heat production is the main driving force of developing new technologies for fuels combustion. Because of the lowest CO₂ emission during the same amount of energy production, methane is viewed as the best fossil fuel for environmental requirements. The catalytic combustion of methane (CCM) becomes a promising approach for decreasing pollutant and also provides wide applications in the industry [1]. Accordingly, approaches have been adopted for preparing catalysts with high activity and stability. These catalysts include precious or promoted transition metals, perovskites and hexaaluminates [1–3].

Comparing with the most efficient precious metal oxide catalysts, copper oxide is considered as a good replacement due to its comparable catalytic performance and low cost [4–6]. Besides, it is well known that ZrO₂ possesses high thermal stability and durability at high temperatures. It was reported that zirconia suppressed the sintering of the active components when they were dispersed mutually [7,8]. Zirconia is also the only metal oxide

with four important chemical properties, namely acidity, basicity, reducing ability and oxidizing ability, thus it is widely used as support for the activation and stabilization of copper oxide [9]. In the past decades, the investigation and modification of zirconia supported copper oxides have been widely carried out. Jackson and Ekerdt [10,11] have confirmed that the oxygen anion vacancy performed as the active site for CO hydrogenation over zirconia or Y₂O₃ doped zirconia. The relationship between the mobility of oxygen and reaction rate was found out. Águila et al. [2] investigated the methane oxidation over copper oxides supported on various solids. They observed that zirconia supported copper oxide was more efficient than the CuO supported on Al₂O₃ and SiO₂. Qu et al. [12] anchored the copper oxide on two kinds of zirconia carriers, demonstrating that the textural structure and property of zirconia carrier greatly affected the catalytic activity for CCM. However, the activity of CuO–ZrO₂ catalysts for CCM was not as excellent as for the other oxidizing reactions. Recently, researchers have endeavored to find approaches for improving the activity of CuO–ZrO₂ catalysts. These investigations are mainly classified as two groups, modifying the chemical and physical properties of the CuO–ZrO₂ catalysts by: (i) adding promoters such as ZnO, CeO₂, and other metal oxides [13–16]; (ii) applying novel preparation methods such as glycine-nitrate combustion synthesis, sol–gel method, surfactant-assisted method [17–20],

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