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Catalytic decomposition of sulfuric acid over CuO/CeO₂ in the sulfur–iodine cycle for hydrogen production

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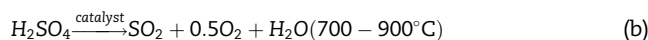
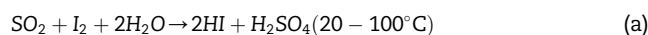
ABSTRACT

The present study is a follow-up of a previous one on a detailed kinetic modeling of the homogeneous decomposition of SO₃–H₂O vapor in the sulfur–iodine cycle for hydrogen production. In this paper, the activity and stability of complex metal oxides Ce_xCu_{1-x}O_{2-δ} prepared by a sol–gel method with x values ranging within 0.2–0.8 were studied for SO₃–H₂O vapor decomposition having a feed rate of space velocity of 5000 ml g⁻¹ h⁻¹ at 727–877 °C. Sample Ce_{0.8}Cu_{0.2}O₂₋₉₀₀ showed even higher activity than Pt catalyst at >800 °C and good stability at 850 °C for 60 h of continuous operation. The physicochemical properties and redox process of CuO/CeO₂ catalysts for SO₃ decomposition were characterized by temperature programmed reduction, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy analyses. A redox mechanism was then proposed based on the characterization results and our previous homogeneous kinetic model. In this mechanism, both ceria-support and copper oxide clusters were reduced, oxidized, and interacted with each other. The overall effect was that CuO/CeO₂ catalyst promoted the reaction of SO₃ + O ↔ SO₂ + O₂, which was the limiting step of SO₃ decomposition, by providing reactive oxygen.

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Introduction

Water is a promising candidate raw material for large-scale hydrogen production, which can help solve the energy problem and reduce greenhouse-gas emissions [1,2]. The sulfur–iodine (SI) cycle with good thermal efficiency and operability is receiving increased attention among the large number of thermochemical water-splitting processes [3]. This SI cycle consists of three steps:



Reaction (a), called the Bunsen reaction, is an exothermic reaction process in liquid phase with an excess of water and iodine that produces two aqueous non-miscible acidic phases,

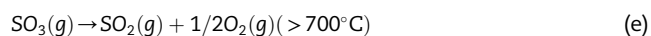
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i.e., the HI_x and sulfuric acids. Reaction (b) is sulfuric acid decomposition that produces O_2 and SO_2 , which is a raw material for the Bunsen reaction. Reaction (c) is hydrogen iodine decomposition that produces H_2 and I_2 , which is also a raw material for the Bunsen reaction. Reaction (b) consists of reactions (d) and (e):



Among the three reactions, H_2SO_4 is easily converted to SO_3 and H_2O [4], but the temperature needed for reaction (e) is very high. Thus, reaction (e) becomes the focus of many research, such as sulfur trioxide electrolysis [4] and the catalytic decomposition of SO_3 using nuclear energy [5].

A catalyst is needed because the direct dissociation rate and conversion ratio of SO_3 is very low at $<900^\circ\text{C}$ [6]. Catalysts can be mainly divided into Pt-based catalysts, transition metal oxides, and complex metal oxides based on the results of previous research. Pt-based catalysts have high activity especially with the carrier of SiC [7–9] even at $<750^\circ\text{C}$. However, their stabilities still need to be improved in long-period tests [10,11]. Single metal oxides such as Fe_2O_3 and CuO can still have high activities with good support [12]. Complex metal oxides appear to be some of the most promising catalysts for SO_3 decomposition because their uniquely high activities even exceed those of Pt-supported catalysts in some cases [9,13–15]. Only a few studies have focused on the mechanism underlying SO_3 decomposition, although metal oxide catalysis is regarded as the repeated reduction–oxidation of metal oxides [16]. Systematic research on the mechanism of catalytic decomposition of SO_3 from homogeneous SO_3 perspective splitting is lacking.

Copper oxide on CeO_2 is known as an efficient catalyst in multiple processes, such as the stabilization and dispersion of noble metals [17], water–gas shift reaction [18,19], SO_2 adsorption [20], and oxidation of CO or methanol [21–23]. Cerium oxides or cerium-based catalysts have high structural oxygen storage and release capacity (OSC) [22,24–27] which is critical to the repeated reduction–oxidation of metal oxides. Nonstoichiometric nanocrystalline CuO/CeO_2 has remarkably higher activity and stability than the corresponding precipitated ultrafine material [24], and these features can be attributed to the formation of a solid solution and dispersion by chemisorption [25,28]. Highly dispersed copper oxide materials are stabilized on the active sites of relatively large nanocrystallines CeO_2 by chemisorption [25,26]. Based on previous CO oxidation research, the incorporation of Cu^{2+} introduces a structural defect (oxygen vacancy) into the CeO_2 lattice and leads to the formation of a solid solution [28]. Thus, the promoted mobility of active oxygen substantially decreases the temperatures related to the reduction or oxidation of copper oxide and cerium oxide [28,29]. Previous research on CO oxidation has some references to SO_3 decomposition. However, research on the catalytic activity of nanocrystalline CuO/CeO_2 for SO_3 decomposition especially at $>700^\circ\text{C}$ has not yet been reported.

Our previous studies have shown that SO_3 homogeneous decomposition encompasses two important elementary

reactions $\text{SO}_3 \leftrightarrow \text{SO}_2 + \text{O}$ and $\text{SO}_3 + \text{O} \leftrightarrow \text{SO}_2 + \text{O}_2$, which involve the release and consumption of active oxygen [6]. CuO/CeO_2 catalysts prepared by sol–gel methods were used for SO_3 decomposition in this study. The effects of calcination temperature and Ce/Cu ratio on SO_3 decomposition ratio were experimentally studied. The physicochemical properties of CuO/CeO_2 catalysts for $\text{SO}_3\text{–H}_2\text{O}$ vapor were characterized by TPR, TEM, XRD, and XPS. The mechanism of SO_3 catalytic decomposition by CuO/CeO_2 catalysts was then proposed according to the characterization results of the aforementioned methods.

Experimental

Catalyst preparation

The Ce/Cu (atomic ratio) values of CuO/CeO_2 catalysts synthesized by sol–gel method were 20 mol%, 50 mol%, and 80 mol%. The nitrates $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ were mixed and stirred with the complex agent sucrose and the dispersant glycol at 90°C in an aqueous solution until a spongy gel remained. The molar ratio of sucrose and glycol to the sum of nitrate $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ was 10:1:5. The gel was then allowed to dry at 110°C for 24 h, carbonized at 400°C for 4 h in N_2 atmosphere, and calcined at 900°C for 3 h or 700°C for 10 h. Finally, the gel was cooled to room temperature in a furnace.

Characterizations

TPR was carried out for unused and used samples on an AutoChem II 2920 Automated Catalyst Characterization System. Exactly 0.04 g of pure copper oxide or complex oxides CuO/CeO_2 was used. The samples were heated under flowing 5% H_2/Ar (30 ml/min) from room temperature to 900°C ($10^\circ\text{C}/\text{min}$). The samples were characterized by TEM using a Tecnai G2 F20 S-TWIN. The powders were ground and dispersed onto molybdenum grids. Powder XRD measurements were recorded with a D/max 2550PC diffractometer. A standard sample holder was used, and measurements were taken within the $10^\circ\text{–}80^\circ$ 2θ range with a step size of 0.02° and step time of 0.02 s. XPS was carried out on an Escalab 250Xi system with Mg $K\alpha$ radiation under UHV (5×10^{-8} Pa), calibrated internally using the carbon deposit C_{1s} with binding energy (BE) of 284.6 eV.

Activity measurement

Sulfuric acid solution with 92.5% concentration was pumped into furnace 1 using a peristaltic pump (BT00-50M) under nitrogen flow at a rate of 60 ml/min controlled with a mass flowmeter, in which preheating, vaporization, and SO_3 generation occurred at 450°C (Fig. 1). Catalyst (1 g) was loaded in a quartz tube-type reactor with a length of 30 cm and a diameter of 1.3 cm in furnace 2, where the catalytic decomposition of SO_3 was performed at $727\text{–}877^\circ\text{C}$ and 1 atm. The exhaust gases went through a spiral condenser, gas-washing bottles, a gas dryer, and an oxygen analyzer. The oxygen concentration

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