



Study on CuO–CeO₂/SiC catalysts in the sulfur–iodine cycle for hydrogen production

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SUMMARY

The structure and activity of ceria–copper oxides supported on nanometer silicon carbide (nano-SiC) particles for sulfuric acid decomposition were studied. The promoting activities and stabilities of CuO–CeO₂ complex oxides loaded on nano-SiC grains were prominently higher than those of CuO–CeO₂ without carriers, especially at <800 °C. The results of X-ray diffraction (XRD), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM) showed that copper–cerium composite oxides grains were well dispersed and fixed on the surface of SiC particle, and the average sizes of CuO–CeO₂ complex oxides carried by SiC particles were considerably smaller than those of CuO–CeO₂ without carriers. Based on the analysis of HRTEM images, X-ray photoelectron spectroscopy (XPS) spectra, and infrared radiation (IR) pattern, the majority of SiC surfaces were converted to SiO₂ layers, in which CeO₂ grains immobilized by coordination bonding Ce–O–Si bridges. From the temperature programmed reduction (TPR) patterns, compared with those of CuO–CeO₂ without carrier, the reduction temperature of CuO to Cu₂O in CuO–CeO₂/SiC catalysts was lowered, especially at (Ce + Cu)/SiC atomic ratio of 5 mol.%. The catalysts also showed relatively high activities at 727 °C for 20 h of continuous operation. A mechanism of SO₃ decomposition on CuO–CeO₂/SiC was proposed according to the characterization results. Copyright © 2016 John Wiley & Sons, Ltd.

KEY WORDS

hydrogen production; sulfur–iodine cycle; sulfuric acid decomposition; CuO–CeO₂/SiC; Ce–O–Si bridges

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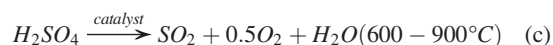
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1. INTRODUCTION

As a promising clean energy, hydrogen can help solve the present energy problem and reduce greenhouse gas emission. In recent years, water is becoming a more and more promising candidate raw material for large-scale hydrogen production without any greenhouse gas emission. Among various methods of hydrogen production from water, thermochemical water splitting cycle is a promising method for large-scale hydrogen production because of its high efficiency. The sulfur–iodine (SI or IS) cycle is one of the most widely researched cycles among more than 100 thermochemical cycles [1,2].

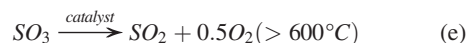
The SI or IS cycle consists of three steps:



In reaction (a) (called the Bunsen reaction), sulfur dioxide that comes from reaction (c) reacts with iodine and water in

liquid phase with an excess of water and iodine, and it produces two non-miscible acidic phases, that is, the HI_x and sulfuric acids. After purification and distillation, as shown in reaction (b), the hydrogen iodine from the HI_x phase is decomposed into hydrogen and iodine. After cooled, the hydrogen is separated from iodine, and iodine is then transported to the reactor of reaction (a) as a reactant. In reaction (c), sulfuric acid that comes from sulfuric acids phase, through purification and concentration, is decomposed into sulfur dioxide, oxygen, and water. The products of reaction (c) are then delivered to the reactor of reaction (a), the sulfur dioxide and water are consumed by reacting with iodine, and the oxygen is separated from others.

Reaction (c) denotes the sulfuric acid decomposition, which consists of two processes, namely, reactions (d) and (e):



H₂SO₄ can be easily converted to SO₃ and H₂O [3], but the temperature needed for SO₃ direct decomposition is extremely high [4].

Catalytic decomposition is the most commonly used method for SO₃ splitting. Catalysts for SO₃ decomposition can be mainly classified into noble metal Pt [5–8] and Ag [9,10], transition metal oxides (Fe₂O₃, CuO, and Cr₂O₃), and complex metal oxides [5,11,12]. The activities of stabilities of Pt-based catalysts can be improved by supporting on excellent carriers, SiC and Al₂O₃, especially at <750 °C [5–8]. However, the high cost of noble metal restricts its large-scale application [13]. Fe₂O₃ catalysts obtain the highest activities among single metal oxides, and the deactivation of Fe₂O₃ is also researched [14–16]. With higher activities and anti-sulfate abilities than single metal oxides, complex metal oxide catalysts appear to be the most promising candidates for Pt catalysts, such as CuCr₂O₄, CuO–V₂O₅, and CuO–CeO₂ [17–20]. Based on recent studies on catalysts, the temperature of reaction (e) can be decreased close to or even lower than 700 °C [7,8,17]. The decomposition temperature of SO₃ over CuO–V₂O₅ can be reduced to 600 °C [17,18], but its stability needs to be verified.

To further improve the activities of various catalysts, the thermodynamic data are thus needed to know the maximum SO₃ conversion ratio. In previous literatures, various evaluations of the SO₃ conversion thermodynamic can be found [3,8,15,21–27]. The systematic studies of SO₃ decomposition show the equilibrium conversion ratio is influenced by pressure and temperature dramatically; thus, the partial pressure of gaseous SO₃ in the reactor needs to be carefully considered when a thermodynamic curve is obtained [3,4,24,25]. The CuO–CeO₂ complex oxides catalyst has been widely used in multiple processes, such as water–gas shift reaction [28], SO₂ adsorption [29], and oxidation of CO or methanol [30,31]. Cerium oxides or cerium-based catalysts have high-structural oxygen storage and release capacity (OSC) [31–33] which is critical to the repeated reduction–oxidation of metal oxides. Based on our previous research, without a carrier, the CuO–CeO₂ complex oxides catalyst is a good catalyst for SO₃ decomposition, and a redox mechanism for SO₃ decomposition over CuO–CeO₂ complex oxides is proposed [19]. However, the stability and activity at <720 °C is still not well. SiC is widely used as support material for catalysts at high temperature and pressure because of its excellent corrosion resistance [7,34].

This study is the first to use CuO–CeO₂ supported on nano-SiC in SO₃ decomposition. The stabilities and activities of CuO–CeO₂/SiC catalysts with different loading ratios and Ce/Cu ratios were investigated. The structural properties of CuO–CeO₂/SiC catalysts were characterized by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), infrared radiation (IR), and temperature programmed reduction (TPR). On the basis of characterization, a mechanism for SO₃ decomposition on CuO–CeO₂/SiC was established.

2. EXPERIMENTAL

2.1. Catalyst preparation

The Ce/Cu atomic ratios of CuO–CeO₂/SiC catalysts synthesized by sol–gel method were 1/1 and 4/1, and the atomic ratios of (Cu + Ce)/Si were 1/19 and 1/9. Nitrate Ce(NO₃)₃ · 6H₂O, Cu(NO₃)₂ · 3H₂O, and nano-SiC powders (average diameter of 40 nm) were mixed and stirred with sucrose and glycol at 90 °C in aqueous solution until a gel remained. The molar ratios of sucrose, glycol, and the sum of nitrate (Ce(NO₃)₃ · 6H₂O and Cu(NO₃)₂ · 3H₂O) and SiC (~40 nm in diameter) were 10:1.5:100 and 10:1.5:50. The concentrations of sucrose, glycol, and the sum of nitrate (Ce(NO₃)₃ · 6H₂O and Cu(NO₃)₂ · 3H₂O) were 0.7 mol L^{−1}, 0.1 mol L^{−1}, and 0.35 mol L^{−1}, respectively. The gel was allowed to dry at 110 °C for 24 h, calcined at 300 °C for 1 h in the air, calcined at 900 °C for 3 h, and cooled in the furnace. Taking catalyst 10 mol.% Ce_{0.5}Cu_{0.5}/SiC as an example, 10 mol.% represents the molar ratio of (Cu + Ce)/SiC, and the active materials CuO–CeO₂ were deposited on SiC.

2.2. Characterization

Powder XRD measurement was performed using a D/max 2550PC diffractometer with Cu K_α radiation (K_α = 1.540598 Å) at 40 kV and 100 mA. XRD patterns were recorded at intervals of 0.02° in the 10°–80° 2θ range. TEM and HRTEM images were taken with a Tecnai G2 F20 S-TWIN. Samples were ground and dispersed onto molybdenum grids. XPS was conducted on an Escalab 250Xi system with Mg K_α radiation under ultra-high vacuum conditions (5 × 10^{−8} Pa). Binding energy (BE) was internally calibrated by carbon deposit C_{1s} at 284.6 eV. The IR spectrum analysis of samples was carried out employing an IR measurement system (Nicolet 5700, Australia). The IR spectra were recorded in the 4000–400 cm^{−1} range with a Nicolet 5700 instrument using the KBr dilution technique. TPR was conducted on an AutoChem II 2920 Automated Catalyst Characterization System. Approximately, 0.05 g of samples was heated under flowing 5% H₂/Ar from room temperature to 800 °C (10 °C/min).

2.3. Activity tests

As shown in Figure 1, sulfuric acid solution (92.5 wt.%, 0.2 mL min^{−1}) was pumped into furnace 1 by using a peristaltic pump (BT00-50 M), preheated, and mixed with nitrogen, which was controlled by a ALICAT mass flow meter at a flow rate of 50 mL min^{−1} at standard condition. The mixture was heated to 500 °C in furnace 1 and holding section, where sulfuric acid decomposed into SO₃ and H₂O. Catalysts weighing 0.5 g were loaded in a quartz tube reactor in furnace 2, where SO₃ was decomposed over catalysts at 677–827 °C with a space velocity of 50 g_{sulfur} · g_{catalyst}^{−1} · h^{−1} and at 1 atm. The mixture from furnace 2 passed through a spiral condenser, gas-washing

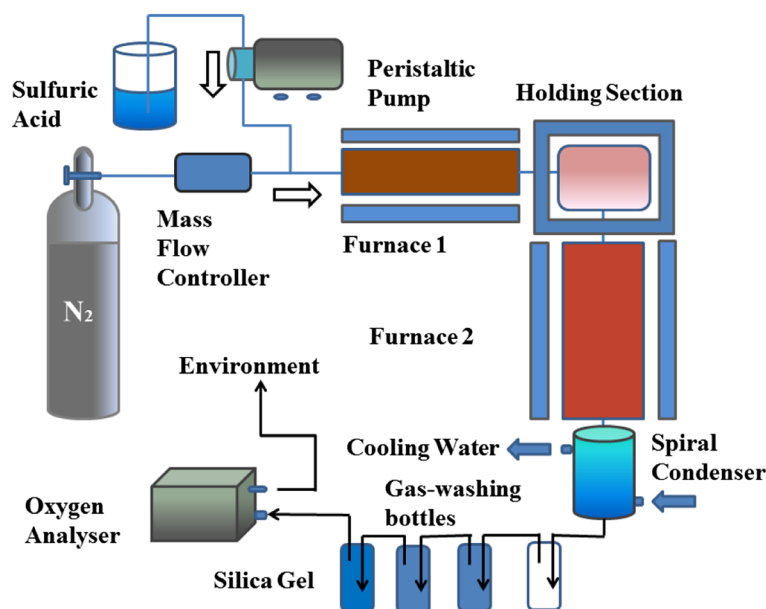


Figure 1. Test rig employed for sulfuric acid decomposition.

bottles, a gas dryer, and an online oxygen analyzer (Repidox-1100Z) in turn. The NaOH solution and silica gel were contained in gas-washing bottles and the gas dryer, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Basic morphological structure of catalysts

TEM (STEM) and XRD were utilized to analyze the morphological structure of the catalysts as shown in Figures 2 and 3. The TEM image of CuO–CeO₂ complex oxides in Figure 2C shows large crystals of approximately 200–1000 nm in diameter, and each particle includes numerous quasi-hexagonal sub-grains (100–200 nm in diameter). Defects, such as cracks and dislocation, were introduced into the ceria crystal in the growing process. A large number of copper oxide particles of size 5–100 nm were uniformly distributed on the surface of ceria crystals in Figure 2C. In Figure 2A and B, the anti-sintering abilities of catalyst samples were markedly improved by deposition on nano-SiC particles, despite the high-calcination temperature at 900 °C. The sizes of ceria crystals (10–50 nm) supported on nanometer SiC were considerably smaller than those of CuO–CeO₂ samples.

The EDX spectra of the 10 mol.% Ce_{0.5}Cu_{0.5}/SiC sample in Figure 2H detected Ce, Cu, Si, and Mo, which are attributed to ceria, copper oxide, SiC, and molybdenum grid. The square in the STEM image of Figure 2F represents a bare region on nano-SiC particles (~40 nm in diameter), and the square in Figure 2G is located on a particle of ~20 nm in diameter. As shown in Figure 2H, the Ce/Si atomic ratio of the square in Figure 2F was 0.05. However, in Figure 2G, the value of Ce/Si ratio increased to as high as 0.76. In addition, the atomic percentage of Cu in

Figure 3D was considerably higher than that in Figure 3B. The bigger dark particle is SiC, and the smaller bright particles on SiC are copper-ceria composite oxide grains. The concentration of copper oxide particles on ceria crystal was higher than that on bare SiC particles, which facilitates the formation of solid solution between ceria and copper oxides. The agglomeration of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC sample was lightly intensified during a 20-h experiment at 727 °C, but the agglomeration of 5 mol.% Ce_{0.5}Cu_{0.5}/SiC was not observed.

The XRD spectra in Figure 3A indicate the presence of CeO₂–cerianite (PDF# 48–1548), CuO–tenorite, and SiC–moissanite. According to the XRD spectra, the average size of CuO–CeO₂ complex oxides was 41.3 ± 3.6 nm in diameter, whereas the sizes of 5 and 10 mol.% Ce_{0.5}Cu_{0.5}/SiC were (20.7 ± 2.3) and (22.64 ± 6.9) nm, respectively. The size calculation from XRD spectra also verified that the average sizes of ceria sub-grains in CuO–CeO₂/SiC samples were smaller than those in CuO–CeO₂ catalysts. In Figure 3B, compared with the Ce_{0.5}Cu_{0.5}O_{1.5–8} sample, the size of copper oxide may be decreased further by observing the broad trend of the bands that belong to CuO. Copper oxide particles that were not directly observed in TEM (STEM) images may be attributed to their small sizes. The particles that were considerably smaller than ceria grains may be copper oxide grains in Figure 2F and G, but the EDX spectra could not be acquired in such small regions. The amorphous tendency of hump curve at ~20° may explain the presence of amorphous SiO₂ on the oxidized surface of SiC particles.

3.2. Comprehensive characterization

The HRTEM image, selected area electron diffraction (SAED) pattern, and XRD pattern in Figure 4 were

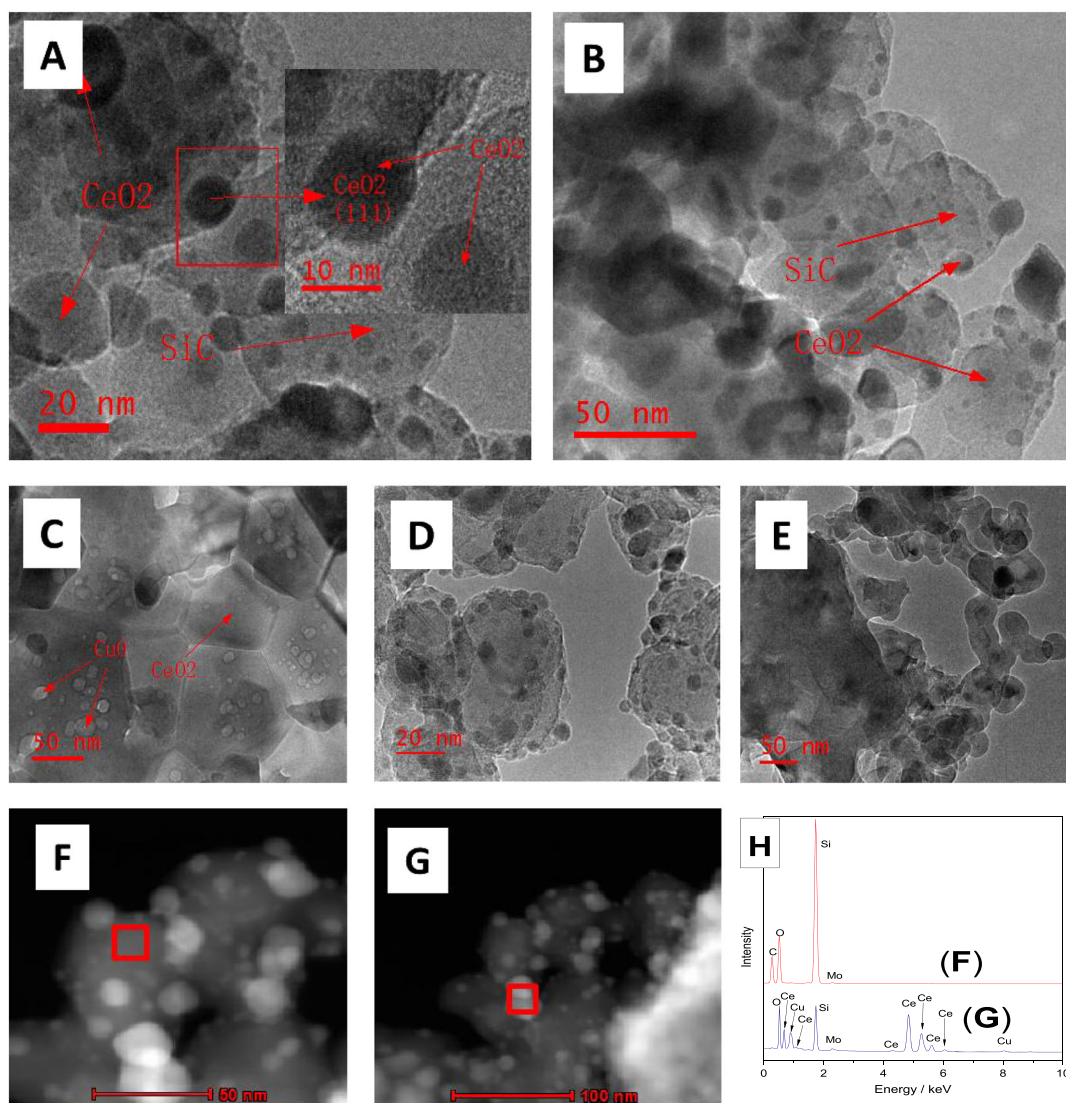


Figure 2. TEM images and XRD profiles of different catalysts. (A) TEM image of 5 mol.% Ce_{0.5}Cu_{0.5}/SiC; (B) TEM image of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC; (C) TEM image of Ce_{0.5}Cu_{0.5}O_{1.5}; (D) TEM image of 5 mol.% Ce_{0.5}Cu_{0.5}/SiC after 20 h experiment; (E) TEM image of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC after 20 h experiment; (F–G) STEM of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC; (H) EDX spectra of square in (F) and (G).

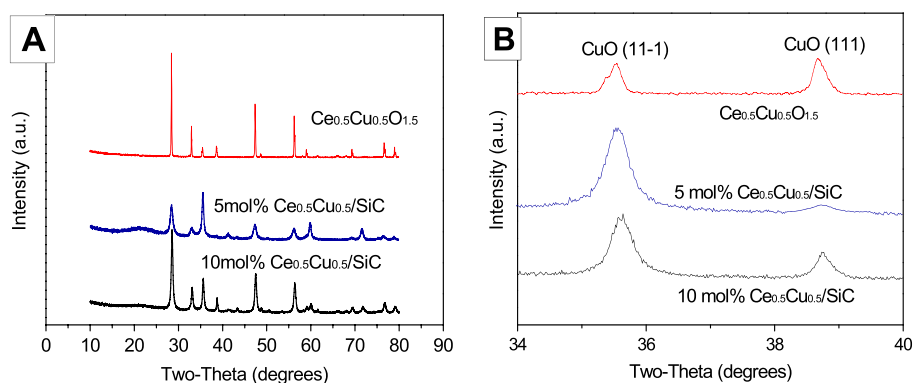


Figure 3. XRD profiles of catalysts Ce_{0.5}Cu_{0.5}O_{1.5}, 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and 10 mol.% Ce_{0.5}Cu_{0.5}/SiC.

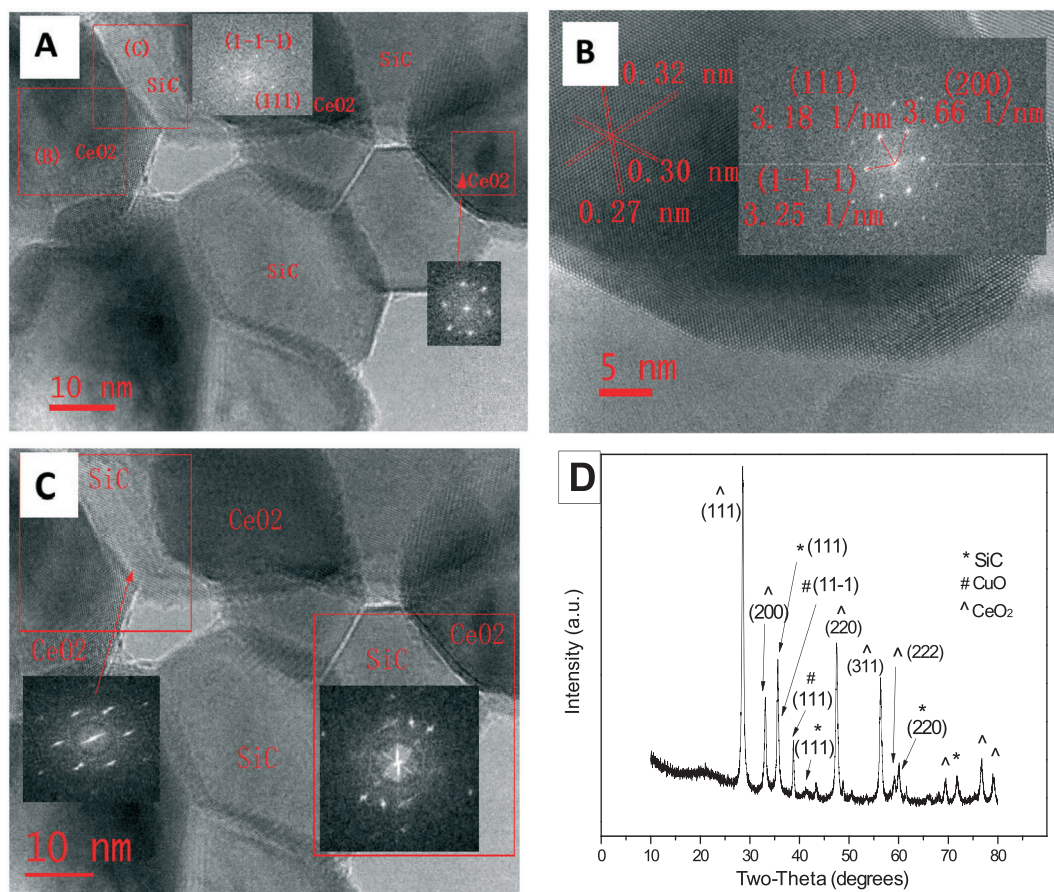


Figure 4. HRTEM images and XRD profiles of different catalysts. (A–C) HRTEM image of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC; (D) XRD profiles of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC.

obtained from 10 mol.% Ce_{0.5}Cu_{0.5}/SiC sample. The HRTEM images in Figure 4 were obtained at a higher magnification than those in Figure 2B to visualize the crystal shapes more clearly and to measure the structure more accurately. The TEM images in Figure 4A and B also proved that the SiC grain surface (~40 nm) was coated with ceria particles. In Figure 4B, the fringe widths were 0.32, 0.27, and 0.31 nm, representing the (111), (200), and (1-1-1) planes of ceria in cubic fluorite, respectively, as proven by XRD pattern in Figure 4D. The peak at ~28.55° in the XRD pattern belonged to low-energy plane CeO₂ (111), which works as an active adsorption site for obtaining an O from adsorbed SO₃ [19]. The dispersed ceria crystal on SiC could not be merged easily; therefore, the number of binding sites of ceria–copper oxides could be largely maintained. The crystal structure of SiC belonged to 3C–SiC according to the XRD patterns. Lattice fringes on SiC could not be observed easily because of the coverage of amorphous SiO₂ layer. In Figure 4C, the diffraction rings in SAED patterns revealed the coexistence of CeO₂ and SiC crystals, as well as the dispersion of ceria grains on SiC particles. However, several comparatively large-size ceria particles existed. No fringe of copper oxide crystals with a tenorite structure was observed in

Figure 4, which can be explained by its considerably smaller size than ceria particles as seen in Figure 3B. As shown in Figure 3A, amorphous SiO₂, which is represented by the lump curve at ~20° in XRD spectra, commonly occurred on the superficial SiC at high temperatures [7,34]. The transformation of superficial SiC to SiO₂ can be observed more directly in the analysis on XPS spectra as follows.

The image in Figure 5 shows the XPS spectra of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC, 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and Ce_{0.5}Cu_{0.5}O_{1.5–δ}. As shown in Figure 5A, the component of the Si_{2p} line at the lower BE side (103 eV) represents the fraction that is due to SiO₂/(SiO₂ + SiC), whereas that at the higher BE side (~103.9 eV) represents the SiO₂ fraction. The high values of O/Si atomic ratio revealed that the majority of superficial SiC particles were converted into SiO₂ during sintering, as shown in Table I. The weak intensity of peaks at ~101 eV represents the fraction of SiC. According to a previous study, the energy difference between O_{1s} and Si_{2p} of SiO₂ lies in the range of 429–430 eV [35]. The energy discrepancy of O_{1s} and Si_{2p} ranged from 429.0 to 430 eV, as observed by comparing Figure 5A and C.

In Figure 5B, the weak peak of C_{1s} at ~283 eV in the 10 mol.% Ce_{0.5}Cu_{0.5}/SiC sample was due to SiC

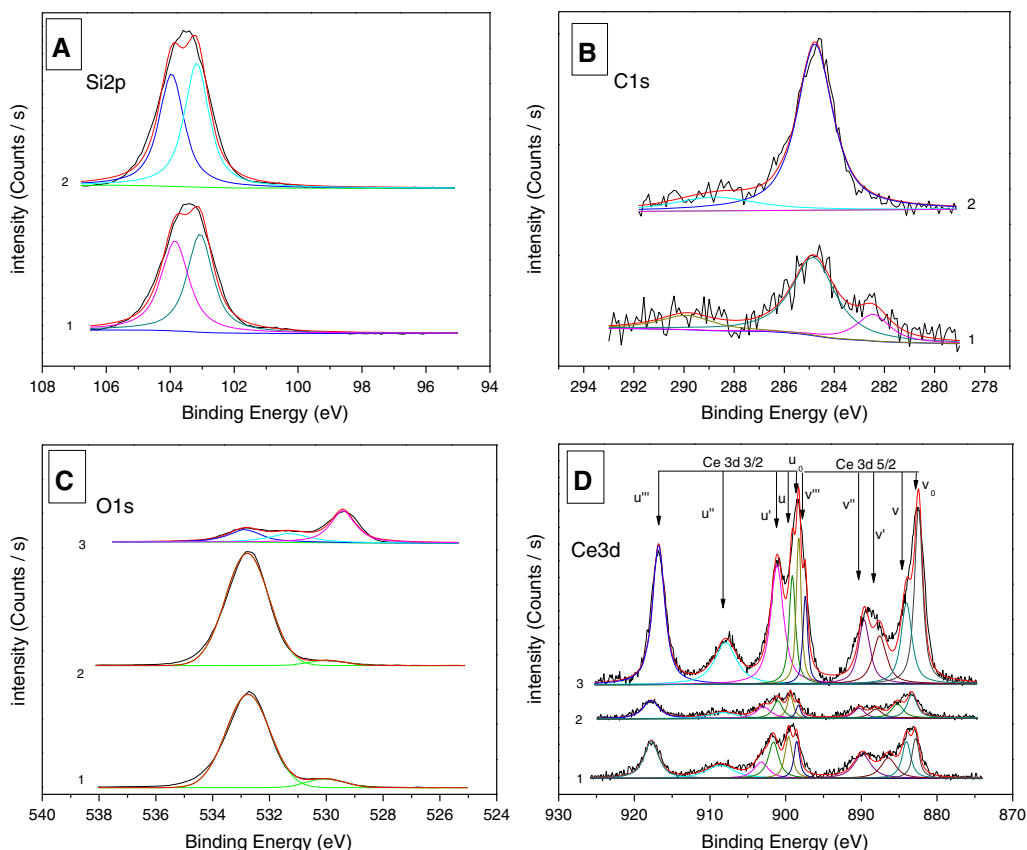


Figure 5. XPS spectra of Si_{2p} (A), C_{1s} (B), O_{1s} (C), and Ce_{3d} (D), where (1) 10 mol.% Ce_{0.5}Cu_{0.5}/SiC, (2) 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and (3) Ce_{0.5}Cu_{0.5}O_{1.5-δ}.

Table I. XPS results measured for the catalysts.

	10 mol.% Ce _{0.5} Cu _{0.5} /SiC			5 mol.% Ce _{0.5} Cu _{0.5} /SiC		
	Atomic %	Ce/Si ratio	O/Si ratio	Atomic %	Ce/Si ratio	O/Si ratio
C _{1s}	4.12			8.28		
Si _{2p}	29.32			28.4		
O _{1s}	63.86	0.051	2.178	62.04	0.021	2.184
Ce _{3d}	1.5			0.61		
Cu _{2p}	1.2			0.67		

[7,35,36]. The C_{1s} component at ~285 eV can be attributed to the free carbon formed by the decomposition of a polymer, hydrocarbon, or contaminant carbon [36], as well as the displaced carbon of the SiC crystal matrix. The weak peak in the range of 288–290 eV was attributed to Si₄C_{4-x}O₂ [36]. The low percentage of carbon from carbide indicates that the surface was largely oxidized, and this finding is consistent with that obtained in the Si_{2p} spectra.

In the O_{1s} spectra as shown in Figure 5C, two different ranges of peaks existed between CuO–CeO₂/SiC and CuO–CeO₂. As for sample CuO–CeO₂ (sample 3), the shoulder peak at ~531.2 eV denotes vacancy defects because of the formation of Cu₂O and Ce₃O₄, whereas the

peaks at ~529.4 eV represent oxygen in ceria crystal [19,37]. The peak at about 533 eV represents the H₂O adsorbed on the catalyst surface. In samples 1 and 2, as shown in Figure 5C, the component of O_{1s} at ~532.4 eV represents SiO₂ on the SiC particle surface, and the peak of O_{1s} at ~533.0 eV denotes SiO₂ [38]. The high ratio of SiO₂/SiC can be observed in the O/Si atomic ratio in Table I. The oxidation process may involve oxygen molecules being adsorbed on the outermost Si layer of the SiC crystal matrix to form C–Si–O bridges. Then, in the process of structural rearrangement during annealing, oxygen atoms displace carbon atoms in superficial SiC layers and preferentially accommodate themselves in those vacant

sites, thus forming SiO₂. The displaced carbon may be another source of the extraneous carbon signal at ~285 eV in SiC. The reason for ceria being fixed on the SiC surface can be related to the oxidized SiO₂ surface.

The spin-orbit of Ce_{3d}, as shown in the XPS spectra in Figure 5D, is split into Ce_{3d3/2} and Ce_{3d5/2}. In the Ce_{3d} spectra of Figure 5D, using overlapping peak resolving, the characteristic peaks of Ce³⁺ are marked v₀, v', u₀, and u', and peaks except for u', u₀, v', and v₀ represent Ce⁴⁺ [39]. Based on the results of peak resolving, the surface Ce³⁺ to Ce_{3d} atomic ratios were 0.33, 0.43, and 0.39 for 10 mol.% Ce_{0.5}Cu_{0.5}/SiC, 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and Ce_{0.5}Cu_{0.5}O_{1.5-δ}, respectively. The high Ce³⁺-to-Ce_{3d} atomic ratios also suggest high concentrations of oxygen defects in the ceria phase, which favors SO₃ decomposition [19].

IR spectroscopy was used to characterize CuO–CeO₂ nanoparticles and CuO–CeO₂/SiC nanoparticles, as shown in Figure 6. The absorption band of CuO–CeO₂ nanoparticles from 1000 to 4000 cm⁻¹ was rather planar, except for peaks at 3435 cm⁻¹, which indicates the O–H stretching vibration of adsorbed H₂O. For CuO–CeO₂, the peak at ~400 cm⁻¹ and shoulder peak at ~525 cm⁻¹ can be regarded as a asymmetric O–Ce–O stretching [40]. CuO–CeO₂/SiC catalysts show the absorption bands, including 1100 and 1220 cm⁻¹ of Si–O–Si asymmetric stretching vibration, 850 cm⁻¹ of Si–O–Si stretching vibration, and 470 cm⁻¹ of Si–O–Si bending vibration [41–43]. The formation of Si–O–Si bridges proved the existence of the SiO₂ layer on the SiC particle surface. Meanwhile, the shoulder peaks of CuO–CeO₂/SiC at 950 cm⁻¹ were due to Si–O–Ce asymmetric vibration [41]. In addition, the bands of CuO–CeO₂/SiC at 1100, 850, and 470 cm⁻¹ shifted to 1060, 810, and 460 cm⁻¹ because of the influence of CeO₂.

The H₂-TPR profiles of copper–ceria oxides can typically be split into three peaks. For example, in Figure 7 and Table II, the first peak in the range of 200–400 °C can be considered as a reduction of small copper oxide clusters and several adsorbed oxygen [33]. The second peak in the range of 400–600 °C belongs to the reduction

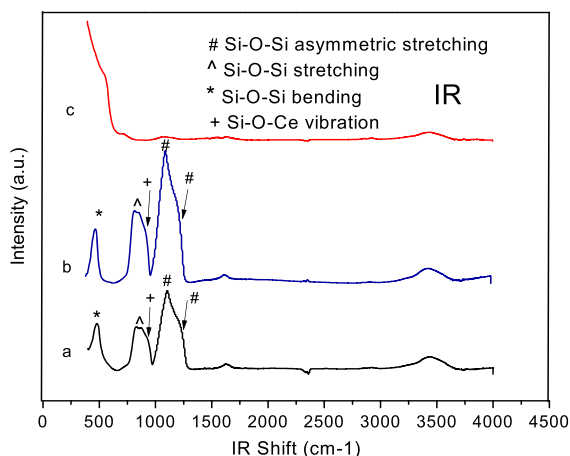


Figure 6. IR spectra of samples, where (a) 10 mol.% Ce_{0.5}Cu_{0.5}/SiC, (b) 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and (c) Ce_{0.5}Cu_{0.5}O_{1.5-δ}.

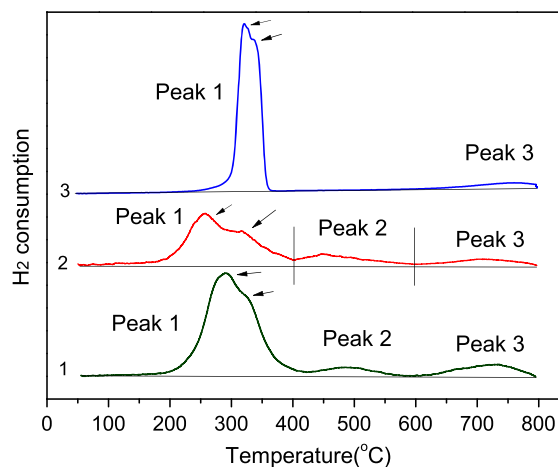


Figure 7. H₂-TPR profiles of different samples, where (1) 10 mol.% Ce_{0.5}Cu_{0.5}/SiC, (2) 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and (3) Ce_{0.5}Cu_{0.5}O_{1.5-δ}.

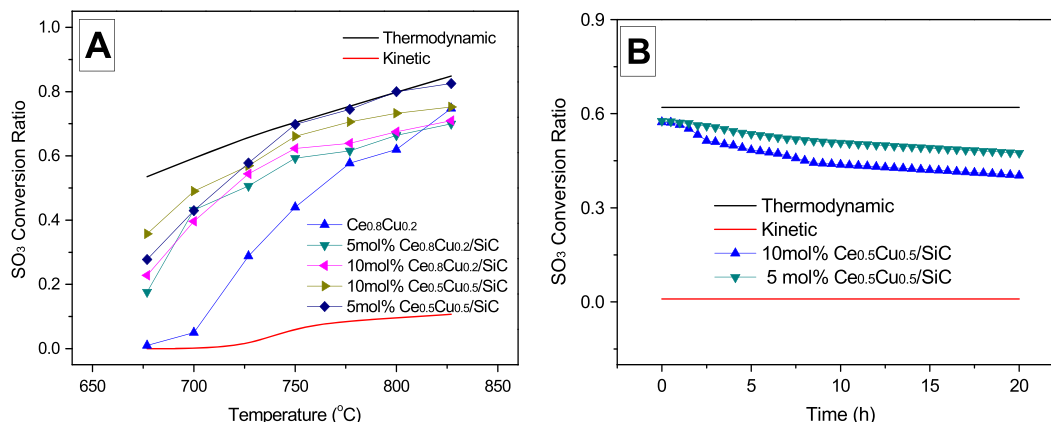
of relatively big copper oxide and the ceria grain surface. The third peak is interpreted as the partial reduction of a deeper layer of crystalline CeO₂ [19,33]. In addition, the main peak of peak 1 represents the reduction of CuO that produces Cu₂O, and the shoulder peak (right) denotes partial reduction of Cu₂O to Cu. The reduction temperature of CuO to Cu₂O is considered an important factor in the SO₃ decomposition mechanism [19]. According to previous studies, the reduction temperature of CuO–CeO₂ complex oxides is lower than those of pure CuO oxide and CeO₂ oxide [19]. The considerably lower reduction temperature of samples 1 and 2 than sample 3 indicates the higher activities of samples 1 and 2. In the range of 600–800 °C, besides reduction in peak 2, 13.29%, 25.32%, and 9.77% of ceria crystals were reduced in samples 10 mol.% Ce_{0.5}Cu_{0.5}/SiC, 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, and Ce_{0.5}Cu_{0.5}O_{1.5-δ}, respectively. Furthermore, the sequence of the reduction temperature of peak 3 from low to high was 5 mol.% Ce_{0.5}Cu_{0.5}/SiC, followed by 10 mol.% Ce_{0.5}Cu_{0.5}/SiC and then Ce_{0.5}Cu_{0.5}O_{1.5-δ}. Therefore, these results prove that, compared with sample Ce_{0.5}Cu_{0.5}O_{1.5-δ}, the activities of 5 mol.% Ce_{0.5}Cu_{0.5}/SiC and 10 mol.% Ce_{0.5}Cu_{0.5}/SiC samples were improved by their smaller copper oxide and ceria particles.

3.3. Catalytic activity

In Figure 8A, the SO₃ conversion ratios over CuO–CeO₂/SiC were close or even higher than those of Pt catalysts [5,7,8]. The SO₃ conversion curve denoted by ‘Thermodynamic’ was obtained by FACTSAGE software [4]. The volumetric flow rate of carrier gas N₂ is 50 mL min⁻¹ in standard condition, and the molar ratio of SO₃/H₂O is 1/1.44. The ‘Kinetic’ curve shows the SO₃ conversion ratio without a catalyst, and it was calculated by CHEMKIN software [4]. Comparing with sample Ce_{0.8}Cu_{0.2}O_{1.8-δ}, the activities of CuO–CeO₂/SiC samples were significantly

Table II. Results of H₂-TPR performed on different catalysts.

Samples	Mass (g)	Mole of CuO (mol)	Mole of CeO ₂ (mol)	H ₂ consumption (mol)		
				Peak 1	Peak 2	Peak 3
10 mol.% Ce _{0.5} Cu _{0.5} /SiC	0.051	4.951×10^{-5}	4.950×10^{-5}	2.601×10^{-5}	0.209×10^{-5}	0.329×10^{-5}
5 mol.% Ce _{0.5} Cu _{0.5} /SiC	0.050	2.730×10^{-5}	2.730×10^{-5}	1.638×10^{-5}	0.193×10^{-5}	0.345×10^{-5}
Ce _{0.5} Cu _{0.5} O _{1.5-δ}	0.054	2.127×10^{-4}	2.127×10^{-4}	13.559×10^{-5}		1.039×10^{-5}

**Figure 8.** (A) SO₃ conversion ratio with complex oxide catalysts of 10 mol.% Ce_xCu_{1-x}/SiC, 5 mol.% Ce_xCu_{1-x}/SiC, and Ce_{0.8}Cu_{0.2}O_{1.5-δ}, where $x = 0.5$ and 0.8 ; (B) stability testing of 10 and 5 mol.% Ce_{0.5}Cu_{0.5}/SiC samples for 20 h at 727 °C.

improved by deposition on nano-SiC, especially at <750 °C. The 10 mol.% Ce_{0.5}Cu_{0.5}/SiC sample presented the highest catalytic activity in the range of 677–727 °C, whereas the activity of 5 mol.% Ce_{0.5}Cu_{0.5}/SiC exhibited the highest activity at 727–827 °C. According to the earlier characterization, the small ceria grains were fixed on SiC particles by Ce–O–Si bridges, and then large numbers of active sites were maintained. In turn, the activities of samples CuO–CeO₂/SiC would be promptly enhanced in the low temperature range. The SO₃ conversion ratios over catalysts were consistent with the characterization results. The SO₃ conversion ratios over CuO–CeO₂/SiC catalysts rapidly increased and could be as high as 0.49 at 700 °C, whereas the SO₃ conversion ratio over sample Ce_{0.8}Cu_{0.2}O_{1.8-δ} (the most active among CuO–CeO₂ catalysts) was still only 0.05 at 700 °C. Among CuO–CeO₂/SiC catalysts, the influence of Ce/Cu atomic ratio on activities increased at >750 °C. Meanwhile, the discrepancy of activities between CuO–CeO₂/SiC and Ce_{0.8}Cu_{0.2}O_{1.8-δ} catalysts decreased with the increase in temperature. The elevated activity of Ce_{0.8}Cu_{0.2}O_{1.8-δ} catalysts could be attributed to further formation of solid solution [19].

As shown in Figure 8B, SO₃ conversion ratios of 5 mol.% Ce_{0.5}Cu_{0.5}/SiC were higher than those of 10 mol.% Ce_{0.5}Cu_{0.5}/SiC within 20 h and at 727 °C. As seen in Figure 2, for the 10 mol.% Ce_{0.5}Cu_{0.5}/SiC sample, sintering existed after 20 h at 727 °C, but the tendency of agglomeration in the 5 mol.% Ce_{0.5}Cu_{0.5}/SiC sample was reduced to a large extent. Activities of the two catalysts gradually

decreased with reaction time, but the SO₃ conversion remained higher than 0.4 at 727 °C.

3.4. Mechanism for SO₃ decomposition

According to previous studies [19], as well as the results of this characterization, a mechanism of SO₃ decomposition over CuO–CeO₂/SiC catalysts was established as shown in Figure 9. According to the kinetic simulation of SO₃ decomposition without catalysts, the reaction rate of SO₃ decomposition was mainly controlled by simple reactions, namely, $\text{SO}_3 = \text{SO}_2 + \text{O}$ and $\text{SO}_3 + \text{O} = \text{SO}_2 + \text{O}_2$ [4]. However, the high values of activation energies of these two reactions restricted the reaction rates [4].

As shown on the left of Figure 9, the SiO₂ layer formed on the oxidized surface of SiC particles. Ceria crystals were immobilized by the SiO₂ layer on SiC particles by Ce–O–Si bridges; thus, further agglomeration among ceria particles was largely prevented. As shown in the bottom-right corner of Figure 9, reaction (1) represented that SO₃ was adsorbed on ceria crystal, forming S–O–Ce bridges by unequal sharing of electrons, and the adsorption sites on the surfaces of CeO_{2-δ} phase take oxygen atoms from SO₃ molecules in reaction (2) [19]. In the upper right corner of Figure 9, given the stability of the 3d atomic orbital of Cu⁺, the reduction process of CuO to Cu₂O occurred at moderately high temperatures (>450 °C) [44]. In reactions (3) and (4), the oxygen atoms from CuO crystals captured by adsorbed SO₃ molecules, decomposing into O₂ and SO₂ molecules. Thus,

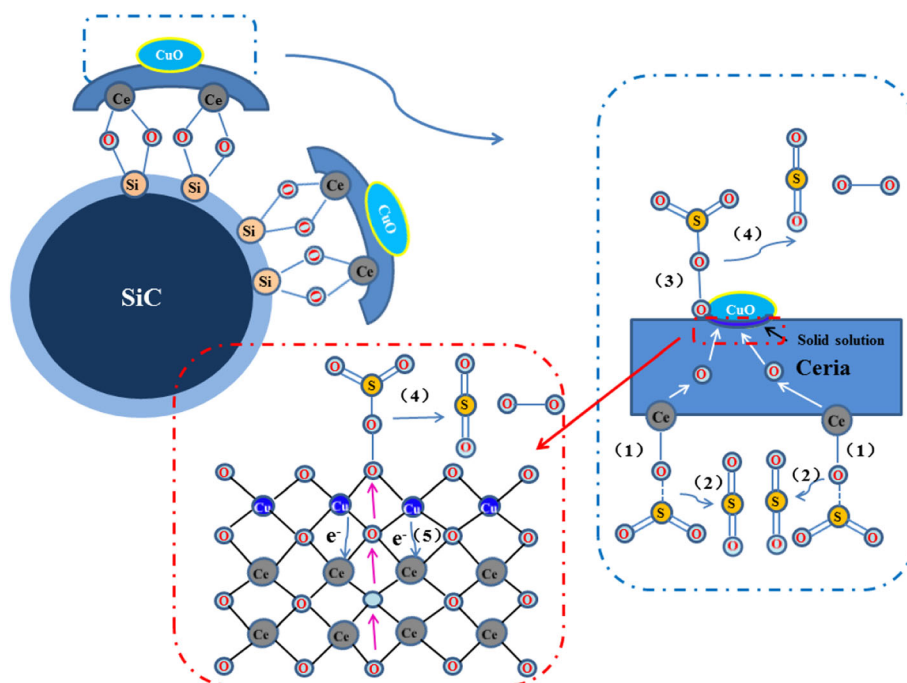
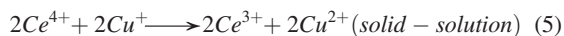
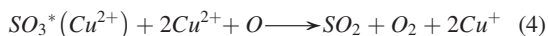
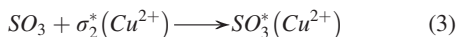
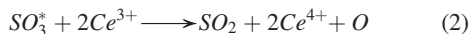
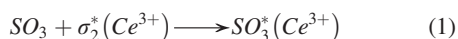


Figure 9. A mechanism for SO₃ decomposition over CuO–CeO₂/SiC catalysts.

the rates of reactions $\text{SO}_3 = \text{SO}_2 + \text{O}$ and $\text{SO}_3 + \text{O} = \text{SO}_2 + \text{O}_2$ were promoted by the earlier processes.

Compared with that in the bulk copper phase, the diffusion of oxygen (or movement of vacancy) was easier in the solid solution region (at the junction between copper oxide and ceria crystals) and CeO_{2–δ} phase [32]. As shown on the right in Figure 9, diffusion of oxygen existed from the ceria surface depriving oxygen to the solid solution region. In the bottom-left corner of Figure 9, the reduction product Cu⁺ was oxidized by Ce⁴⁺, that is, the redox equilibrium of reaction (5) $\text{Ce}^{4+} + \text{e}^- = \text{Ce}^{3+} + \text{Cu}^{2+}$ [45]. Ce³⁺ was then re-oxidized by the oxygen atom through diffusion, and another SO₃ molecule reacted with oxygen atom that was released by CuO. Finally, the reaction rate of SO₃ decomposition was accelerated in the presence of CuO–CeO₂/SiC catalysts. The processes are expressed by reactions (1–5):



4. CONCLUSIONS

In the SI cycle, the decomposition temperature of SO₃ was further reduced by CuO–CeO₂/SiC catalysts, even in comparison with the highly-active Ce_{0.8}Cu_{0.2}O_{1.8–δ} catalysts.

The stability of 5 and 10 mol.% Ce_{0.5}Cu_{0.5}/SiC catalysts were not good enough to maintain for 20 h and at 727 °C. The effects of Ce/Cu ratio and (Cu + Ce)/Si ratio were also investigated. The Ce/Cu ratio of 1/1 was more suitable for a favorable catalytic performance when the atomic ratio of (Cu + Ce)/Si ranged from 5 to 10 mol.%.

TEM (HRTEM), XRD, XPS, IR, and TPR characterizations were used to investigate the structure and redox characters of the CuO–CeO₂ complex oxides on nano-SiC particles. Morphology that small copper-ceria composite oxide particles fixed on nano-SiC grains was obtained by TEM (HRTEM) and XRD. The composition and chemical state of each element of catalysts were analyzed by XPS, which proved the existence of a thin SiO₂ layer on the SiC particle surface. The formation of Ce–O–Si bridges was revealed by IR spectra. H₂-TPR profiles showed that the reduction temperature of CuO–CeO₂/SiC catalysts was considerably lower than that of the Ce_{0.8}Cu_{0.2}O_{1.8–δ} catalyst. Based on the results of characterization and redox mechanism of CuO–CeO₂, a mechanism of SO₃ decomposition over CuO–CeO₂/SiC catalysts was proposed. However, the decomposition of CuO–CeO₂/SiC sulfate at low temperature remained unclear, and the mechanism still needed to be verified.

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