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Reaction behaviors of CH<sub>3</sub>CN catalytic combustion over CuCeO<sub>x</sub>-HZSM-5 composite catalysts: The mechanism of enhanced N<sub>2</sub> selectivity

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#### **Graphical abstract**



#### Highlights

- High N<sub>2</sub> selectivity was achieved on CuCeO<sub>x</sub>-HZSM-5 composite catalysts.
- The introduction of HZSM-5 enhanced the hydrolysis of CH<sub>3</sub>CN and NCO(a).
- The enhanced  $N_2$  selectivity could be attributed to the internal SCR reaction.
- The synergism between  $CuCeO_x$  and HZSM-5 facilitated the internal SCR reaction.

#### Abstract:

In this paper, the reaction behaviors of CH<sub>3</sub>CN catalytic combustion over CuCeO<sub>*x*</sub>-HZSM-5 catalysts prepared by the physical mixing and wet impregnation methods

were investigated. The experimental results had revealed that the composite catalysts exhibited excellent degradation efficiency and high N<sub>2</sub> selectivity: the Cu-Ce oxides ensured the high activity, and the introduction of HZSM-5 limited the formation of NO<sub>x</sub>. The involved reaction mechanism was then studied by an *in situ* DRIFT analysis. It could be deduced that different reaction pathways would occur over CuCeO<sub>x</sub> and HZSM-5. The catalytic reaction over CuCeO<sub>x</sub> mainly proceeded via an oxidation pathway. The CN group could be converted to isocyanate species [NCO(a)] which would be further oxidized to NO<sub>x</sub>. Over HZSM-5, CH<sub>3</sub>CN was mainly hydrolyzed into ammonia. For the CuCeO<sub>x</sub>-HZSM-5 composite catalysts, the overoxidation of NCO(a) and NH<sub>3</sub> was inhibited, and an internal selective catalytic reduction (SCR) reaction could occur, thereby greatly improving the N<sub>2</sub> selectivity. **Keywords: Acetonitrile; CuCeO<sub>x</sub>; HZSM-5; Catalytic combustion; N<sub>2</sub> selectivity** 

#### **1** Introduction

Volatile organic compounds (VOCs) have received widespread attentions as major precursors of ozone and secondary organic aerosols [1]. As one category of highly toxic VOCs, the emission of cyanide-containing waste gases, such as acetonitrile and acrylonitrile, have become a serious threaten to human health [2]. Incineration and catalytic combustion are the most promising methods for eliminating VOCs. However, the incineration of cyanide-containing gas would normally lead to high levels of secondary pollution (NO<sub>x</sub>) emissions and high energy costs [3, 4]. As such,

catalytic combustion has been recognized as one of the most suitable methods for cyanide-containing gas abatement due to its low operating temperature and less secondary pollution [5].

Currently, there are still few reports focused on the catalytic combustion of cyanidecontaining gases. The noble metal catalysts had showed excellent low-temperature activities, but their N<sub>2</sub> selectivity was not satisfactory. For instance, Pt/Al<sub>2</sub>O<sub>3</sub> catalysts had exhibited a total HCN conversion of 95% at temperatures above 250 °C, while the N<sub>2</sub> selectivity was found to be less than 30% [6]. Adsorbed NCO species have been proposed to be important intermediates for the oxidation of CN groups, which could be rapidly converted to NO<sub>x</sub> and N<sub>2</sub>[7]. Similar research results were presented for the catalytic combustion of CH<sub>3</sub>CN [8]. Moreover, due to the superiorities in terms of their economic efficiency, transition metal oxide catalysts were also employed for cyanide-containing compound catalytic combustion in several previous studies [4, 9, 10]. Although superior activities were obtained, NO<sub>x</sub> formation at high temperatures was still a problem.

Meanwhile, cyanide-containing compounds could hydrolyze over some catalysts, including TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and HZSM-5 [11]. For example, the hydrolysis of acrylonitrile proceeds over zeolite catalysts to form acetic acid and NH<sub>3</sub> [12]. However, these abovementioned catalysts possessed an insufficient deep oxidation ability. This fact motivated the design of a composite catalyst possessing both a high activity and a good N<sub>2</sub> selectivity, in which (1) one component comprised materials such as transition metal oxides with a high activity for the deep oxidation of a cyanide-

containing gas and (2) the other component possessed a hydrolysis functionality to produce NH<sub>3</sub> for reducing NO<sub>x</sub> via an internal SCR reaction cycle. In this work, Cu-Ce mixed oxides were selected as the main oxidation component, since such catalysts were widely reported for their excellent activities in CO oxidation and VOC catalytic abatement, owing to the good reducibility induced by copper-cerium interactions [13-15]. Additionally, HZSM-5 zeolites were employed herein as the component used to facilitate the hydrolysis process due to their advantages of high specific surface areas, abundant acidic sites and good thermal stabilities [16]. Moreover, transition metalmodified zeolites have shown a satisfactory activity and N<sub>2</sub> selectivity for NH<sub>3</sub> selective oxidation and NH<sub>3</sub>-SCR reactions [17, 18].

In this paper, acrylonitrile (CH<sub>3</sub>CN) was selected as the target pollutant. In addition, the CH<sub>3</sub>CN catalytic combustion performances (including the activity, CO<sub>2</sub> yield and N-containing byproduct yield) over CuCeO<sub>x</sub>-HZSM-5 composite catalysts synthesized by physical mixing and wet impregnation methods were investigated. After that, various characterization studies were performed to reveal the reaction behaviors of CH<sub>3</sub>CN catalytic combustion and the intrinsic mechanism regarding the structure-performance relationship.

#### **2 Experimental**

#### **2.1 Materials**

HZSM-5 zeolites were purchased from Tianjin Zeolite Plant of Nankai University (China). The Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (AR), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (AR) and citric acid (AR) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). Deionized water was used in all experiments.

#### 2.2 Catalyst preparation

The CuCeO<sub>x</sub> catalyst was prepared via the following synthesis method.

Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were used as the precursors of the copper and cerium species, respectively, with a molar ratio Cu/(Cu+Ce) of 0.5. First, the two precursors were added to a citric acid solution to achieve a molar ratio of the citric acid/metal components of 1.3 and a molarity (Cu+Ce) of 0.6 M. The mixture was continuously stirred for 4 h. Then, the solution was dried at 120 °C for approximately 20 h and calcined at 500 °C for 4 h in static air.

The CuCeO<sub>x</sub>-HZSM-5 composite catalysts were prepared by physical mixing and traditional impregnation methods. CuCeO<sub>x</sub>+HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=18, 27, 300) was prepared by mechanically mixing the CuCeO<sub>x</sub> catalyst and HZSM-5 zeolite at a weight ratio of 1/1. CuCe/ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=27) was prepared by a traditional impregnation method. The detailed procedures were as follows: HZSM-5 was impregnated by the Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O mixture. Similarly, the molar ratio of Cu/(Cu+Ce) was 0.5, and the mass ratio of CuCeO<sub>x</sub> and HZSM-5 was 1/1. The drying and calcining procedures were the same as the procedures used to prepare CuCeO<sub>x</sub>.

#### 2.3 Catalysts characterizations

The BET analysis was conducted using a nitrogen adsorption apparatus (JW-BK132F, China) to obtain the specific surface areas, pore volume and pore size of the catalysts. XRD was conducted using an X-ray diffractometer (model D/max RA, Rigaku Co., Japan; Cu Kα radiation, 0.154118 nm) to determine the crystal phases of the catalysts.

X-ray photoelectron spectroscopy (XPS) was performed with Al Ka X-rays (Thermal, ESCALAB 250, USA) to determine the chemical states of the catalyst surface atoms. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) was conducted using a custom-made multipurpose adsorption instrument (TP-5089, Tianjin Xianquan Co., Ltd., China) equipped with a thermal conductivity detector (TCD) and a mass spectrometer (Hiden Analytical Ltd., UK). For the H<sub>2</sub>-TPR experiments, 0.05 g of the samples were pretreated in a flow of O<sub>2</sub>/He at 400 °C for 1 h, and then, the temperature was cooled to 30 °C. At 30 °C, the He flow was switched to a flow of 6% H<sub>2</sub>/N<sub>2</sub>, after which the temperature was increased from 30 °C to 800 °C at a rate of 10 °C/min. The temperature-programmed surface reaction of CH<sub>3</sub>CN (CH<sub>3</sub>CN-TPSR) and NH<sub>3</sub> (NH<sub>3</sub>-TPSR) was also carried out on a TP-5089 device. For the CH<sub>3</sub>CN-TPSR experiments, 0.75 g of the samples were pretreated in a flow of O<sub>2</sub>/He at 400 °C for 1 h, and then, the temperature was cooled to 30 °C. At 30 °C, the O<sub>2</sub>/He flow was switched to a flow of 600 ppm CH<sub>3</sub>CN (200 ppm NH<sub>3</sub> for the NH<sub>3</sub>-TPSR), 5% O<sub>2</sub> and He as a carrier gas (60 mL/min) for 1.5 h. Thereafter, the temperature was increased from 30 °C to 700 °C at a rate of 5 °C/min, and the data were recorded with a mass spectrometer. In situ DRIFT was conducted using a Nicolet 6700 FT-IR spectrometer equipped with an MCT detector. The catalysts were pretreated in a flow of He at 300 °C for 1 h in the cell and then cooled to the corresponding temperature (100 °C, 250 °C or 350 °C) to obtain the background. Thereafter, the IR spectra were collected at different times in a flow of 600 ppm CH<sub>3</sub>CN with 5% O<sub>2</sub>/He.

#### 2.4 Activity measurements

The catalytic activity tests were performed in a fixed-bed microreactor at atmospheric

pressure. To investigate the effect of each component on the activity and selectivity of the composite catalysts, 0.625 g of the individual catalysts or 1.25 g of the composite catalysts (40-60 mesh) were loaded in a quartz tube reactor. The flow rate of the reactant gas was 1000 mL/min, which corresponds to W/F=0.0375 or 0.075 gs/mL. The reactant gas consisted of ca. 600 ppm CH<sub>3</sub>CN, 5% O<sub>2</sub> and N<sub>2</sub> as a balance gas. The inlet and outlet concentration of CH<sub>3</sub>CN were analyzed online by a gas chromatograph with an FID, while CO<sub>2</sub> was analyzed with a nickel conversion furnace and an FID. The concentration of NO and NO<sub>2</sub> were analyzed with an infrared gas analyzer (MGA5, MRU Co., Germany); the concentration of N<sub>2</sub>O was analyzed by another flue gas analyzer (G200, Geotech Co., UK); the effluent stream containing NH<sub>3</sub> was first absorbed in a 0.01 M H<sub>2</sub>SO<sub>4</sub> solution. Then, the concentration of NH<sub>3</sub> was determined by Nessler's reagent spectrophotometry. The N<sub>2</sub> selectivity was not directly determined, as N<sub>2</sub> is not detectable by infrared gas analyzers. It is feasible to evaluate the N2 selectivity by calculating the yield of Ncontaining byproducts (NH<sub>3</sub>, NO, NO<sub>2</sub> and N<sub>2</sub>O). The conversion of CH<sub>3</sub>CN and the yield of CO<sub>2</sub>, NH<sub>3</sub>, NO, NO<sub>2</sub> and N<sub>2</sub>O were defined as follows:

$$Conversion of CH_3CN = ([CH_3CN]_{in} - [CH_3CN]_{out}) / [CH_3CN]_{in} \times 100\%$$
(1)

#### **3 Results and discussions**

#### **3.1 Catalytic performances**

The catalytic degradation efficiencies and yield of the products (including CO<sub>2</sub>, NH<sub>3</sub> and NO<sub>x</sub>) for CH<sub>3</sub>CN catalytic combustion over different samples were presented in **Fig. 1**. It was found that CuCeO<sub>x</sub> had the highest activity, and CH<sub>3</sub>CN could be completely converted at 225 °C. The activities of CuCeO<sub>x</sub>+HZSM-5 and CuCe/ZSM-5 were lower than that of the CuCeO<sub>x</sub> sample. In addition, no conversion of CH<sub>3</sub>CN could be observed on pure HZSM-5 until 350 °C was reached. The CO<sub>2</sub> yield profile depicted in **Fig. 1b** shows that the variations of the CO<sub>2</sub> yield fitted well with the results of the activity. The CO<sub>2</sub> yield of all the samples except pure HZSM-5 could approach 90% at temperatures above 250 °C.

The NO<sub>x</sub> yield of all the samples is shown in Fig. **1c.** Over the CuCeO<sub>x</sub> sample, the yield of NO<sub>x</sub> rapidly increased when the temperature increased to greater than 200 °C. For instance, a NO<sub>x</sub> yield of more than 40% was achieved at 275 °C. Thereafter, the yield of NO<sub>x</sub> was slowly increasing with increased temperatures. After introducing HZSM-5, the NO<sub>x</sub> yield of the CuCeO<sub>x</sub>+HZSM-5 and CuCe/ZSM-5 samples decreased dramatically. For the CuCe/ZSM-5 sample, the NO<sub>x</sub> yield was less than 10% within the temperature range of 150-400 °C. As shown in **Fig. 1d**, NH<sub>3</sub> could form over CuCeO<sub>x</sub> at lower temperatures, while the NH<sub>3</sub> formation over HZSM-5 could be detected at higher temperatures, which may be due to HZSM-5 having quite a low activity. The yield of NH<sub>3</sub> over CuCeO<sub>x</sub> and CuCeO<sub>x</sub>+HZSM-5 displayed a maximum value at 200 °C. From 200 to 250 °C, the yield of NH<sub>3</sub> decreased, and the yield of NO<sub>x</sub> increased simultaneously. It could be speculated that the oxidation of NH<sub>3</sub> could be one of the sources of NO<sub>x</sub>. However, the decreased NH<sub>3</sub> emissions did

not lead to an evident increase in the NO<sub>x</sub> formed over the CuCe/ZSM-5 sample. Additionally, the stability test of the CuCe/ZSM-5 sample was carried out at 250 °C for 18 h, as illustrated in **Fig. S1**, which confirmed the very good stability of the catalyst.

#### **3.2 Physical property analysis**

Table 1 shows the textural properties of the different samples, including the BET surface area, pore volume and pore size. It could be observed that  $CuCeO_x$  (41.3)  $m^2/g$ ) possessed a mesoporous structure, whose pores were much larger than those of the HZSM-5-related samples. In addition, the CuCe/ZSM-5 and CuCeO<sub>x</sub>+HZSM-5 catalysts had higher BET surface areas compared to the CuCeO<sub>x</sub> sample, owing to the HZSM-5 support having a much larger surface area  $(370.3 \text{ m}^2/\text{g})$  than the CuCeO<sub>x</sub> sample. Compared with the physically mixed sample, CuCe/ZSM-5 had a lower surface area and smaller pore volume, because more metal species migrated and accumulated inner the HZSM-5 microchannel [19]. Fig. 2 illustrated the XRD patterns of all the samples. For the CuCeO<sub>x</sub> sample, the diffraction peaks located at 28.5°, 33.1°, 47.5° and 56.3° could be ascribed to CeO<sub>2</sub> with a fluorite-like structure (JCPDS 81-0792). In addition, the two diffraction peaks located at 35.6° and 38.8° were assigned to CuO (JCPDS 89-8599). For HZSM-5, the diffraction peaks located at 23.0°, 23.9°, 24.3°, 26.9°, 29.9°, 45.0° and 45.6° could be ascribed to the characteristic MFI-type framework of HZSM-5 (JCPDS 79-2401) [20, 21]. For the composite catalysts, the peaks corresponding to CeO<sub>2</sub> and CuO could be clearly observed. And the MFI-type framework of HZSM-5 was preserved, indicating that

metal loading will not change the structure of the HZSM-5 support.

#### 3.3 Reducibility and surface properties

The H<sub>2</sub>-TPR experiments were conducted for the CuCeO<sub>x</sub>-HZSM-5 catalysts to evaluate the reducibility of various samples. As shown in Fig. 3, the CuCeO<sub>x</sub> and CuCeO<sub>x</sub>+HZSM-5 samples exhibited two reduction peaks at the lower temperature range. Based on the previous studies [22-24], the peak located at 150-160 °C could be attributed to finely dispersed Cu species strongly interacting with CeO<sub>2</sub>, and the peak located at ~200 °C could be attributed to larger CuO clusters on the surface of CeO<sub>2</sub>. For CuCe/ZSM-5, the first peak located at ~200 °C could be attributed to the reduction of larger CuO clusters that are less associated with CeO<sub>2</sub> or isolated Cu<sup>2+</sup> ions, and the other peak at approximately 250 °C could be assigned to the reduction of large CuO particles [25, 26]. It is well known that Cu<sup>2+</sup> resulted from the Cu ions occupying the ion-exchange sites of HZSM-5 [21]. The strong interaction between the Cu species and the HZSM-5 support would weaken the Cu-Ce interactions, leading to the lower reducibility of the CuCe/ZSM-5 sample. For pure HZSM-5, no obvious reduction peak was observed within the temperature range investigated, suggesting the absence of reducible oxygen species. The H2-TPR results were in good accordance with the activity results.

To further investigate the surface atomic states, XPS characterization was then carried out. **Fig. 4A** shows the Cu 2p core level spectra for the CuCeO<sub>x</sub>-HZSM-5 samples. For all the samples, the Cu  $2p_{3/2}$  peak located at ~933.5 eV and the corresponding shake-up satellites located at 941-943.4 eV confirmed the appearance of bulk-like

CuO. In addition, the peak located at ~935.8 eV could be ascribed to  $Cu^{2+}$  that was bound to weak oxygen species [27, 28]. Particularly, for CuCe/ZSM-5, the peak located at ~935.8 eV could be ascribed to isolated  $Cu^{2+}$  that was tetrahedrally coordinated in the HZSM-5 framework. It could be found that more  $Cu^{2+}$  species existed on the CuCe/ZSM-5 sample, which confirmed the strong interaction between the Cu species and the support. For the CuCeO<sub>x</sub> and CuCeO<sub>x</sub>+HZSM-5 samples, the Cu 2p<sub>3/2</sub> peak located at 932.5 eV could be ascribed to Cu<sup>+</sup> [29]. Additionally, the presence of Cu<sup>+</sup> indicated the strong interaction between CuO and CeO<sub>2</sub> [13], which was consistent with the high reducibility of the CuCeO<sub>x</sub> and CuCeO<sub>x</sub>+HZSM-5 samples, as shown by the H<sub>2</sub>-TPR results [30].

The Ce 3d core level spectra are shown in Fig. **4B**. The curves of the Ce 3d spectra were composed of ten peaks, and the "v" with "u" peaks represented the spin orbit split  $3d_{5/2}$  and  $3d_{3/2}$  states, respectively. The doublets (u<sub>0</sub>, u') and (v<sub>0</sub>, v') were assigned to Ce<sup>3+</sup>, while the other peaks were assigned to Ce<sup>4+</sup> [31, 32]. The O 1S core level spectra was shown in Fig. **4C**. The peak ( $\alpha$ ) at ~529.6 eV could be ascribed to the lattice oxygen (O<sub>tott</sub>) of the metal oxides. In addition, the peak ( $\beta$ ) at 530.6-531.5 eV could be ascribed to the adsorbed oxygen (O<sub>ads</sub>) [19, 33]. For the CuCeO<sub>x</sub> sample, the peak ( $\gamma$ ) at ~532.7 eV could be attributed to the oxygen in the hydroxyl groups [34]. Meanwhile, the peak ( $\gamma$ ) could be attributed to the oxygen of the HZSM-5 support of the composite catalysts [19, 35]. The surface Ce<sup>3+</sup>/Ce<sup>4+</sup> and O<sub>ads</sub>/O<sub>latt</sub> molar ratios were calculated from the Ce 3d and O 1S curve-fittings, respectively, and the result is shown in **Table 1**. The Ce<sup>3+</sup>/Ce<sup>4+</sup> ratios decreased in the order of CuCeO<sub>x</sub>+HZSM-5

 $(0.176) \approx \text{CuCeO}_x (0.172) > \text{CuCe/ZSM-5} (0.138)$ , and the relative abundance of  $O_{ads}$  followed the same order. In general, the abundant Ce<sup>3+</sup> species and  $O_{ads}$  will be beneficial to the reducibility, thereby promoting the CH<sub>3</sub>CN degradation reactivity [36]. Besides the catalytic activity, N<sub>2</sub> selectivity was also very important to CH<sub>3</sub>CN catalytic combustion. Therefore, the reaction process was investigated in the following section to determine the relative mechanism of the enhanced N<sub>2</sub> selectivity over the composite catalysts.

#### 3.4 TPSR of CH<sub>3</sub>CN oxidation

As shown in **Fig. 5**, the oxidation behaviors of CH<sub>3</sub>CN and the formation of the Ncontaining products over all the samples were further investigated by the TPSR technique. Over the CuCeO<sub>x</sub> sample, the concentration of CH<sub>3</sub>CN began to decrease at temperatures above 200 °C, and N<sub>2</sub>, NH<sub>3</sub> and NO<sub>x</sub> subsequently formed. N<sub>2</sub>O was the main byproduct within the temperature range of 200 to 300 °C, while at higher temperatures, large amounts of NO formed at elevated temperatures. Compared to CuCeO<sub>x</sub>, the composite samples showed an evident decrease in the CH<sub>3</sub>CN concentration at higher temperatures, suggesting their lower activity. However, it was found that N<sub>2</sub> was the main product that formed over the two composite samples. Obviously, the introduction of HZSM-5 limited the formation of NO<sub>x</sub> and improved the N<sub>2</sub> selectivity over the composite catalysts, which was consistent with the results of the activity tests. Additionally, more NO emissions formed over CuCeO<sub>x</sub>+HZSM-5 at temperatures over than 400°C compared to the impregnated sample. For the pure HZSM-5 sample, the rapid oxidation of CH<sub>3</sub>CN was detected at temperatures greater

than 350 °C, and small amounts of NO<sub>x</sub> formed. To further disclose the reaction mechanism responsible for the different N-containing product formation behaviors, *in situ* DRIFT measurements were then conducted.

#### **3.5 DRIFT Measurements**

#### 3.5.1 CH<sub>3</sub>CN + O<sub>2</sub> coadsorption over HZSM-5

Fig. 6 shows the DRIFT spectra of the adsorption of 600 ppm CH<sub>3</sub>CN with 5% O<sub>2</sub> over HZSM-5 for various times and at different temperatures. At 100 °C (see Fig. 6a), due to the adsorption of CH<sub>3</sub>CN, a series of IR bands emerged, and their intensities grew gradually. The bands at 2278 and 2306 cm<sup>-1</sup> could be ascribed to the vCN FR doublet of the CH<sub>3</sub>CN molecules interacting with strong H-bonding. In addition, the band at 2326 cm<sup>-1</sup> could be attributed to the vCN FR doublet of the CH<sub>3</sub>CN molecules coordinated on the Al<sup>3+</sup> cations, and its resonance peak was overlapped with the band at 2278-2306 cm<sup>-1</sup>. The band at 2939 cm<sup>-1</sup> could be assigned to CH<sub>3</sub> stretching [37]. The sources of the bands at 1286 and 1184 cm<sup>-1</sup> were ambiguous and needed further identification. In addition, several weak bands at 1695, 1666 and 1585 cm<sup>-1</sup> could also be detected and may be derived from the hydrolysis of acetonitrile. According to a previous study [12], CH<sub>3</sub>CN was hydrolyzed by a twostep process: acetamide formed first and was then rapidly hydrolyzed to release ammonia and acetic acid. As such, the bands at 1666 and 1585 cm<sup>-1</sup> could be ascribed to the C=O stretching and NH<sub>2</sub> bending of acetamide, respectively [38]. In addition, the band at 1695 cm<sup>-1</sup> was attributed to the adsorbed molecules of acetic acid [39]. As the temperature increased, as shown in Fig. 6b and 6c, the absorbance of the bands at 2278, 2306, 2326, and 2939 cm<sup>-1</sup> decreased, which was due to the limited adsorption

and the catalytic conversion of CH<sub>3</sub>CN at high temperatures. At the same time, it was found that the absorbance of the bands at 1666 and 1585 cm<sup>-1</sup> owing to acetamide initially increased and then decreased. Additionally, the absorbance of the band (1695 cm<sup>-1</sup>) attributed to acetic acid was observed to increase rapidly with increasing temperatures. All these abovementioned results indicated the increased rate of the CH<sub>3</sub>CN hydrolysis reaction at higher temperatures. In addition, the appearance of two broad bands with rapidly increasing intensities at 3384 and 3294 cm<sup>-1</sup> with increasing temperatures further confirmed it, which were attributed to adsorbed NH4<sup>+</sup> and NH3 molecules, respectively [5, 40]. Moreover, the intensities of the bands at 1286 and 1184 cm<sup>-1</sup> were observed to decrease initially at 250 °C and then increase at 350 °C, which was accompanied by their positions shifting to 1288 and 1176 cm<sup>-1</sup>, respectively. Due to the ammonia and acetic acid formed from the hydrolysis reaction at high temperatures, these two bands may be related to the formation of ammonia and acetic acid. To further identify these two bands, the DRIFT spectra of HZSM-5 exposed to 600 ppm NH<sub>3</sub> at 250 °C was then obtained. As shown in Fig. S2, similar IR bands of adsorbed NH<sub>3</sub> located at 1288 and 1176 cm<sup>-1</sup> could be detected. Based on the literatures [41, 42], both bands appearing at high temperatures in Fig. 6 could be attributed to the symmetric bending vibrations of the N-H bonds in coordinately adsorbed NH<sub>3</sub>. Bands located at 1286 and 1184 cm<sup>-1</sup> appeared as soon as CH<sub>3</sub>CN adsorbed at low temperatures, and these bands were possibly due to the CN groups interacting with H-bonding. Therefore, the absorbance of the bands located at 1286 and 1184 cm<sup>-1</sup> decreased initially at an elevated temperature as less CH<sub>3</sub>CN adsorbed.

At 350 °C, new faint bands appeared at 1520 and 2202 cm<sup>-1</sup>, which could be ascribed to amide (-NH<sub>2</sub>) species and weakly adsorbed NO, respectively [42].

 $3.5.2 \text{ CH}_3\text{CN} + O_2 \text{ coadsorption over CuCeO}_x$ 

Fig. 7 shows the DRIFT spectra of the adsorption of CH<sub>3</sub>CN in the presence of 5% O<sub>2</sub> over CuCeO<sub>x</sub> for various reaction times and at different temperature. As shown in Fig. **7a**, the bands at 2258 and 2293 cm<sup>-1</sup> could be ascribed to the vCN FR doublet of CH<sub>3</sub>CN interacting with Lewis acid sites. The bands at 2931 and 2999 cm<sup>-1</sup> could be assigned to CH<sub>3</sub> stretching [37]. The cleavage of the C-H bond of CH<sub>3</sub>CN led to the formation of CH<sub>2</sub>CN species, and the band at 2120 cm<sup>-1</sup> proved the formation of CH<sub>2</sub>CN species [43]. In the 1150-1660 cm<sup>-1</sup> frequency range, a series of bands at 1556, 1529, 1471, 1427, 1207 and 1178 cm<sup>-1</sup> appeared, which could be attributed to the formation of acetamide monoanions [CH<sub>3</sub>CONH(a)] owing to the interaction between CH<sub>3</sub>CN and the surface hydroxyl groups [43-45]. In addition, the bands at 1653 and 3330 cm<sup>-1</sup> were due to the C=O vibration of CH<sub>3</sub>COO(a) and vNH of CH<sub>3</sub>CONH(a) [43], respectively. When the temperature increased to 250 °C, as shown in Fig. 7b, the band at 2120 cm<sup>-1</sup> disappeared, and the absorbance of the bands at 1653, 1529, 1471, 1207 and 1178 cm<sup>-1</sup> significantly decreased. New bands appeared at 2170, 1602, 1344, 1234, 2360 and 2331 cm<sup>-1</sup>. The band at 2170 cm<sup>-1</sup> could be ascribed to NCO ionically bounded to metal cation [46]. Additionally, the band at 1602 cm<sup>-1</sup> was attributed to the formation of NO<sub>2</sub> species [47] or bridged nitrate species [48], indicating the formation of NO<sub>x</sub>. Furthermore, the band at 1344  $\text{cm}^{-1}$ could be assigned to bidentate carbonates [49], as well as the emission of CO<sub>2</sub> (the bands located at 2360 and 2331 cm<sup>-1</sup>) [50]. These results verified that the catalytic

oxidation reaction occurred over the CuCeO<sub>x</sub> sample. The NH<sub>3</sub> observed on catalytic performance may result from the hydrolysis of CH<sub>3</sub>CONH(a), and the weak band at 1234 cm<sup>-1</sup> could be ascribed to NH<sub>3</sub> coordinated on the Lewis acid sites [51]. By further increasing the temperature to 350 °C, all the peaks attributed to the CH<sub>3</sub>CONH(a) groups vanished, and the intensity of the new bands at 1375 cm<sup>-1</sup> and in the 1560-1450 cm<sup>-1</sup> range, which are attributed to surface nitrate species [42, 52] dramatically increased, suggesting that a large amount of NO<sub>x</sub> would be released at high temperatures. As such, it could be concluded that the over oxidation of NCO(a) was the main cause of NO<sub>x</sub> formation. In addition, the band at 2306 cm<sup>-1</sup> could also be ascribed to NCO(a) species [53].

3.5.3 DRIFT of  $CH_3CN + O_2$  coadsorption over the composite catalysts

To determine the mechanism of the improved N<sub>2</sub> selectivity over the CuCeO<sub>x</sub>-HZSM-5 composite catalysts, DRIFT spectra of the coadsorption of CH<sub>3</sub>CN with 5% O<sub>2</sub> over CuCeO<sub>x</sub>+HZSM-5 and CuCe/ZSM-5 were obtained at 250 °C. As illustrated in **Fig. 8a**, the bands at 2322 and 2293 cm<sup>-1</sup> could ascribed to adsorbed CH<sub>3</sub>CN molecules. Additionally, the bands attributed to adsorbed CH<sub>3</sub>CONH<sub>2</sub> (1664 cm<sup>-1</sup>), CH<sub>3</sub>COOH (1695 cm<sup>-1</sup>), NH<sub>x</sub> species (3384, 3294 and 3273 cm<sup>-1</sup>), CH<sub>3</sub>CONH(a) (1558, 1427 and 1178 cm<sup>-1</sup>) and carbonates (1344 cm<sup>-1</sup>) could also be detected on CuCeO<sub>x</sub>+HZSM-5, and these bands corresponded to the bands (1666, 1695, 3384 and 3294 cm<sup>-1</sup>) observed for the HZSM-5 sample and the bands (1556, 1427, 1178 and 1344 cm<sup>-1</sup>) observed for the CuCeO<sub>x</sub> sample. In addition, the bands at 1543 and 1439 cm<sup>-1</sup> could also be assigned to CH<sub>3</sub>CONH(a) [45]. Compared to the CuCeO<sub>x</sub> spectrum, the band at 2170 cm<sup>-1</sup> attributed to NCO(a) nearly vanished, and the band attributed to HNCO

 $(2264 \text{ cm}^{-1})$  appeared, which indicated the migration of NCO(a) from CuCeO<sub>x</sub> to HZSM-5. A similar phenomenon was observed over the Cu-ZSM-5 catalyst [53]. Moreover, the band at  $1602 \text{ cm}^{-1}$  disappeared, which indicated a decrease in the number of NO<sub>2</sub> species or bridged nitrate species formed over CuCeO<sub>x</sub>, suggesting that less NO<sub>x</sub> formed. For the CuCe/ZSM-5 sample shown in Fig. 8b, the bands attributed to adsorbed CH<sub>3</sub>CONH<sub>2</sub> (1662 and 1585 cm<sup>-1</sup>), CH<sub>3</sub>COOH (1695 cm<sup>-1</sup>), NH<sub>x</sub> species (3380 and 3273 cm<sup>-1</sup>), CH<sub>3</sub>CONH(a) (1558, 1456, 1421, 1371 and 1163 cm<sup>-1</sup>) and HNCO (2264 cm<sup>-1</sup>) could also be observed. It is found that the catalytic reaction occurring over CuCe/ZSM-5 was similar to that occurring over CuCeO<sub>x</sub>+HZSM-5, and the latter reaction was more intense, since the intensity of the IR bands due to CO<sub>2</sub> (2360 and 2390 cm<sup>-1</sup>) were relatively stronger compared with that of the band attributed to adsorbed CH<sub>3</sub>CN. Moreover, the relatively stronger IR bands attributed to the hydrolysis intermediates indicated that the hydrolysis reaction was more readily to happen over the CuCeO<sub>x</sub>+HZSM-5 sample due to its stronger acidity compared to CuCe/ZSM-5 sample (see Fig. S3).

#### 3.6 Mechanism of CH<sub>3</sub>CN catalytic decomposition

Based on the results of the activity tests, the characterization studies (especially the DRIFT study) and previous studies [3, 5, 11], the CH<sub>3</sub>CN decomposition mechanism over the different catalysts were concluded. It is proposed that the CH<sub>3</sub>CN decomposition that occurred over HZSM-5 and CuCeO<sub>x</sub> followed different reaction pathways. The hydrolysis of CH<sub>3</sub>CN was the predominant reaction that occurred over the HZSM-5 sample. During the hydrolysis reaction, the protonation of CH<sub>3</sub>CN and

water nucleophilic attack proceed [12]. CH<sub>3</sub>CONH<sub>2</sub> was the only hydrolysate in the first step of CH<sub>3</sub>CN hydrolysis. Subsequently, CH<sub>3</sub>CONH<sub>2</sub> rapidly hydrolyzed to form NH<sub>3</sub> and CH<sub>3</sub>COOH. The reaction pathway (hydrolysis pathway) over HZSM-5 could be described as follows:

$$CH_3CN + H_2O \rightarrow CH_3CONH_2$$
 (5)

$$CH_3CONH_2 + H_2O \rightarrow NH_3 + CH_3COOH$$
 (6)

However, little NH<sub>3</sub> emissions were detected during the activity tests at temperatures below 300 °C. A possible reason for the minor NH<sub>3</sub> emissions could be attributed to the poor redox capacity of HZSM-5 inhibiting the further oxidation of the hydrolysis products. Therefore, the hydrolysis reactions were limited at low temperatures. At temperatures higher than 350 °C, the hydrolysis reaction extent increased greatly over the HZSM-5 sample, in which CH<sub>3</sub>COOH and NH<sub>3</sub> were further oxidized via the following reaction pathways:

$$NH_3 + O(a) \rightarrow N_2 \text{ or } NO_x + H_2O$$
 (7)

$$CH_3COOH + O(a) \rightarrow CO_2 + H_2O$$
(8)

Differing from the hydrolysis process that occurred over the HZSM-5 sample, CH<sub>3</sub>CN would first interact with the surface hydroxyl groups on CuCeO<sub>x</sub> to form CH<sub>3</sub>CONH(a) groups [45]. The CH<sub>3</sub>CONH(a) species could be further hydrolyzed to ammonia at low temperature. However, as the temperature increased, the hydrolysis reaction was limited and CH<sub>3</sub>CONH(a) species were rapidly oxidized to NCO(a) species which could be further oxidized to form large amounts of NO<sub>x</sub>. Therefore, NH<sub>3</sub> yield reached a maximum value at 200 °C over CuCeO<sub>x</sub> and CuCeO<sub>x</sub>+HZSM-5

samples. In addition, it has been widely accepted that NCO species can react with NO, O<sub>2</sub> or NO+O<sub>2</sub> to produce N<sub>2</sub> at high temperature [54], which explained that the amount of NO<sub>x</sub> formed over CuCeO<sub>x</sub> increased slowly when the temperature was increased from 275 to 400 °C. The reaction pathway (oxidation pathway) over CuCeO<sub>x</sub> can be described as follows:

$$CH_{3}CN + OH(a) \rightarrow CH_{3}CONH(a)$$

$$CH_{3}CONH(a) + O(a) \rightarrow NCO(a) + CO_{2} + H_{2}O$$

$$NCO(a) + O(a) \rightarrow N_{2} \text{ or } NO_{x} + CO_{2}$$

$$(11)$$

As for the CuCeO<sub>x</sub>-HZSM-5 composite catalysts, both hydrolysis and oxidation reactions would happen. In addition to these two pathways, NO<sub>x</sub> formed from the oxidation of NCO(a), which could react with the NH<sub>3</sub> formed by the hydrolysis of CH<sub>3</sub>CN via an internal SCR reaction, thereby improving the N<sub>2</sub> selectivity. Furthermore, the NCO(a) groups could migrate to HZSM-5 to form HNCO, and HNCO would be subsequently hydrolyzed into CO<sub>2</sub> and NH<sub>3</sub> [55], which could also participate in the internal SCR reaction to reduce NO<sub>x</sub>. In addition, the NH<sub>3</sub>-TPSR results (see **Fig. S4**) revealed that the introduction of HZSM-5 could inhibit the overoxidation of NH<sub>3</sub> to form NO<sub>x</sub> and improve the N<sub>2</sub> selectivity. For the composite catalysts, HZSM-5 could provide abundant Brønsted acid sites. According to literatures [56, 57], the strong Brønsted acidity could suppress the over-oxidation of NH<sub>3</sub> and thereby increase the accessibility for the reduction of nitrogen oxides. Therefore, it could be concluded that both internal SCR reaction and selective catalytic oxidation (SCO) of NH<sub>3</sub> to N<sub>2</sub> could effectively occur over the composite

catalysts to enhance the  $N_2$  selectivity. All the reaction pathways regarding the enhanced  $N_2$  selectivity were listed below:

$$NCO(a) + H^+ \rightarrow HNCO \tag{12}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{13}$$

$$NH_3 + NOx + O(a) \rightarrow N_2 + H_2O (SCR)$$
(14)

$$NH_3 + O(a) \rightarrow N_2 + H_2O (SCO)$$
(15)

The activity tests (see Fig. 1) indicated that CuCe/ZSM-5 maintained a good N<sub>2</sub> selectivity in a broad temperature range, while the CuCeO<sub>x</sub>+HZSM-5 sample generated some NO<sub>x</sub> emissions at high temperatures. This fact may be attributed to the interaction between  $CuCeO_x$  and HZSM-5 in the physically mixed sample being weaker compared to that in the impregnation sample. Over the CuCeO<sub>x</sub>+HZSM-5 sample, NCO(a) may not migrate to the surface of HZSM-5 in time and was rapidly oxidized to NO<sub>x</sub> at high temperatures. Furthermore, the better reducibility of this sample (see the H<sub>2</sub>-TPR results in Fig. 3) may also led to the over-oxidation of ammonia to release NO<sub>x</sub> at high temperatures. Overall, it could be concluded that the Cu-Ce mixed oxides could ensure the CH<sub>3</sub>CN catalytic decomposition activity, while the high redox ability of the Cu-Ce mixed oxides would lead to the over-oxidation of nitrogen-containing intermediates [NCO(a) and NH<sub>3</sub>], which would release large amounts of NO<sub>x</sub> and lower the N<sub>2</sub> selectivity. Additionally, the introduction of HZSM-5 would enhance the hydrolysis of CH<sub>3</sub>CN and NCO(a), thereby inhibiting the overoxidation of NCO(a) and improving the N<sub>2</sub> selectivity via internal SCR reactions. In addition, the strong acidity of HZSM-5 could also suppress the over-oxidation of NH<sub>3</sub>

to NO<sub>x</sub> at an elevated temperature, promoting the NH<sub>3</sub> SCO reaction over the composite catalysts. The relative mechanism of the enhanced N<sub>2</sub> selectivity over the composite catalysts was presented in **Fig. 9**. Such a mechanism could be further verified by performing activity tests over the CuCeO<sub>x</sub> sample that was physically mixed with HZSM-5 using different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. As shown in **Fig. 10**, it was found that the introduction of HZSM-5 at lower silica contents would lead to less NO<sub>x</sub> formation. HZSM-5 zeolites with lower silica contents possessed more Brønsted acid sites, which would enhance the inhibition effect on NH<sub>3</sub> over-oxidation [57]. In addition, such improved acidity would also promote the hydrolysis of CH<sub>3</sub>CN and NCO(a).

#### 4 Conclusion

In this paper, the CH<sub>3</sub>CN catalytic combustion performances were investigated over CuCeO<sub>x</sub> and CuCeO<sub>x</sub>-HZSM-5 composite catalysts. The catalytic performances indicated that the CuCeO<sub>x</sub>-HZSM-5 composite catalysts showed satisfactory catalytic activities and formed less NO<sub>x</sub>, and CH<sub>3</sub>CN could be converted completely at 250 °C with a NO<sub>x</sub> yield of less than 10%. Compared to pure CuCeO<sub>x</sub> sample, it is found that the introduction of HZSM-5 significantly limited the formation of NO<sub>x</sub> and improved the N<sub>2</sub> selectivity. In particular, the CuCe/ZSM-5 sample showed an excellent N<sub>2</sub> selectivity over a boarder temperature range. Based on the *in situ* DRIFT analysis, it could be concluded that the CH<sub>3</sub>CN decomposition occurred over CuCeO<sub>x</sub> followed an oxidation pathway (CH<sub>3</sub>CN  $\rightarrow$  CH<sub>3</sub>CONH(a)  $\rightarrow$ NCO(a) groups  $\rightarrow$  N<sub>2</sub>/NO<sub>x</sub>,

CO<sub>2</sub>), while the CH<sub>3</sub>CN decomposition that occurred over HZSM-5 proceeded via a hydrolysis pathway (CH<sub>3</sub>CN  $\rightarrow$  CH<sub>3</sub>CONH<sub>2</sub>  $\rightarrow$  CH<sub>3</sub>COOH, NH<sub>3</sub>). For the CuCeO<sub>x</sub>-HZSM-5 composite catalysts, the promotional effect of HZSM-5 introduction on the N<sub>2</sub> selectivity can be explained by an internal SCR mechanism, in which the NO<sub>x</sub> derived from the over-oxidation of NCO(a) on CuCeO<sub>x</sub> could be reduced by the NH<sub>3</sub> formed by the CH<sub>3</sub>CN hydrolysis reaction that occurred over HZSM-5. In addition, the migration of the NCO(a) intermediate from CuCeO<sub>x</sub> to HZSM-5 improved the hydrolysis of HNCO to NH<sub>3</sub>, which would also inhibit the oxidation of NCO(a). Moreover, the NH<sub>3</sub>-TPSR experiment showed that the introduction of strongly acidic HZSM-5 could also inhibit the over-oxidation of NH<sub>3</sub> at high temperatures. Compared to the physically mixed sample, CuCe/ZSM-5 exhibited a better N<sub>2</sub> selectivity owing to the stronger interaction between CuCeO<sub>x</sub> and HZSM-5, which was beneficial to the hydrolysis reaction and internal SCR reaction.

#### **Author Contributions**

Yuxing Wang: Investigation, Writing- Original draft preparation. Yue Liu:
Supervision, Writing- Reviewing and Editing. Qingji Ying: Investigation. Yaoyu
Zhang: Formal analysis. Zhongbiao Wu: Resources, Writing- Reviewing and Editing.

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#### Reference

- [1] W. Wu, B. Zhao, S. Wang, J. Hao, Journal of environmental sciences. 53 (2017) 224-237.
- [2] R. Zhang, D. Shi, N. Liu, B. Chen, L. Wu, L. Wu, W. Yang, Catalysis Today. 258 (2015) 17-27.
- [3] T. Nanba, S. Masukawa, J. Uchisawa, A. Obuchi, Journal of Molecular Catalysis A: Chemical.
   276 (2007) 130-136.
- [4] R. Zhang, P. Li, R. Xiao, N. Liu, B. Chen, Applied Catalysis B: Environmental. 196 (2016) 142-154.
- [5] R. Zhang, D. Shi, N. Liu, Y. Cao, B. Chen, Applied Catalysis B: Environmental. 146 (2014) 79-93.
- [6] H. Zhao, R.G. Tonkyn, S.E. Barlow, B.E. Koel, C.H.F. Peden, Applied Catalysis B:Environmental. 65 (2006) 282-290.
- [7] P. Dagaut, P. Glarborg, M. Alzueta, Progress in Energy and Combustion Science. 34 (2008) 1-46.
- [8] G. Karakas, A. Sevinc, Catalysis Today. 323 (2019) 159-165.
- [9] C. Du, H. Chen, X. Zhao, H. Zong, X. Zhou, Catalysis Communications. 123 (2019) 27-31.
- [10] Y. Hu, J. Liu, J. Cheng, L. Wang, L. Tao, Q. Wang, X. Wang, P. Ning, Applied Surface Science.427 (2018) 843-850.
- [11] O. Kröcher, M. Elsener, Applied Catalysis B: Environmental. 92 (2009) 75-89.
- [12] L.A.M.M. Barbosa, R.A. van Santen, Journal of Catalysis. 191 (2000) 200-217.
- [13] S. Sun, D. Mao, J. Yu, Z. Yang, G. Lu, Z. Ma, Catalysis Science & Technology. 5 (2015) 3166-3181.
- [14] G. Zhou, H. Lan, T. Gao, H. Xie, Chemical Engineering Journal. 246 (2014) 53-63.

- [15] T. Tsoncheva, G. Issa, T. Blasco, M. Dimitrov, M. Popova, S. Hernández, D. Kovacheva, G.
- Atanasova, J.M.L. Nieto, Applied Catalysis A: General. 453 (2013) 1-12.
- [16] P. Yang, S. Zuo, R. Zhou, Chemical Engineering Journal. 323 (2017) 160-170.
- [17] A.C. Akah, G. Nkeng, A.A. Garforth, Applied Catalysis B: Environmental. 74 (2007) 34-39.
- [18] T. Zhang, J. Liu, D. Wang, Z. Zhao, Y. Wei, K. Cheng, G. Jiang, A. Duan, Applied Catalysis B: Environmental. 148-149 (2014) 520-531.
- [19] Z. Zhu, G. Lu, Z. Zhang, Y. Guo, Y. Guo, Y. Wang, ACS Catalysis. 3 (2013) 1154-1164.
- [20] Q. Dai, W. Wang, X. Wang, G. Lu, Applied Catalysis B: Environmental. 203 (2017) 31-42.
- [21] L. Pang, C. Fan, L. Shao, K. Song, J. Yi, X. Cai, J. Wang, M. Kang, T. Li, Chemical Engineering Journal. 253 (2014) 394-401.
- [22] G. Avgouropoulos, T. Ioannides, H. Matralis, Applied Catalysis B: Environmental. 56 (2005) 87-93.
- [23] T. Caputo, L. Lisi, R. Pirone, G. Russo, Applied Catalysis A: General. 348 (2008) 42-53.
- [24] C. Wang, Q. Cheng, X. Wang, K. Ma, X. Bai, S. Tan, Y. Tian, T. Ding, L. Zheng, J. Zhang, X. Li, Applied Surface Science. 422 (2017) 932-943.
- [25] S. Fan, J. Xue, T. Yu, D. Fan, T. Hao, M. Shen, W. Li, Catalysis Science & Technology. 3 (2013)2357.
- [26] W. Huang, Y. Liu, Z. Wu, Catalysis Communications. 122 (2019) 58-62.
- [27] I. Platzman, R. Brener, H. Haick, R. Tannenbaum, Journal of Physical Chemistry C. 112 (2008) 1101-1108.
- [28] M. Piumetti, S. Bensaid, T. Andana, N. Russo, R. Pirone, D. Fino, Applied Catalysis B: Environmental. 205 (2017) 455-468.

- [29] P. Liu, E.J. Hensen, Journal of the American Chemical Society. 135 (2013) 14032-14035.
- [30] M. Konsolakis, Applied Catalysis B: Environmental. 198 (2016) 49-66.
- [31] R. Leppelt, B. Schumacher, V. Plzak, M. Kinne, R. Behm, Journal of Catalysis. 244 (2006) 137-152.
- [32] D. Mrabet, A. Abassi, R. Cherizol, T.-O. Do, Applied Catalysis A: General. 447-448 (2012) 60-66.
- [33] Q. Zou, Y. Zhao, X. Jin, J. Fang, D. Li, K. Li, J. Lu, Y. Luo, Applied Surface Science. 494 (2019)1166-1176.
- [34] T. Gu, Y. Liu, X. Weng, H. Wang, Z. Wu, Catalysis Communications. 12 (2010) 310-313.
- [35] X. Dong, W. Shen, Y. Zhu, L. Xiong, J. Shi, Advanced Functional Materials. 15 (2005) 955-960.
- [36] P. Dutta, S. Pal, M.S. Seehra, Y. Shi, E.M. Eyring, R.D. Ernst, Chemistry of Materials. 18 (2006) 5144-5146.
- [37] G. Busca, T. Montanari, M. Bevilacqua, E. Finocchio, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 320 (2008) 205-212.
- [38] C.-C. Chuang, W.-C. Wu, M.-X. Lee, J.-L. Lin, Physical Chemistry Chemical Physics. 2 (2000) 3877-3882.
- [39] M.A. Hasan, M.I. Zaki, L. Pasupulety, Applied Catalysis A: General. 243 (2003) 81-92.
- [40] L. Wang, W. Li, G. Qi, D. Weng, Journal of Catalysis. 289 (2012) 21-29.
- [41] R.Q. Long, R.T. Yang, Journal of Catalysis. 194 (2000) 80-90.
- [42] L. CHEN, J. LI, M. GE, Environmental science & technology. 44 (2010) 9590-9596.
- [43] A. ABOULAYT, C. BINET, J. LAVALLEY, Journal of The Chemical Society-faraday

Transactions. 91 (1995) 2913-2920.

[44] L.F. Liao, C.F. Lien, D.L. Shieh, F.C. Chen, J.L. Lin, Physical Chemistry Chemical Physics. 4

(2002) 4584-4589.

- [45] M. Tamura, A. Satsuma, K.-i. Shimizu, Catalysis Science & Technology. 3 (2013) 1386.
- [46] Y. Yeom, B. Wen, W. Sachtler, E. Weitz, Journal Of Physical Chemistry B. 108 (2004) 5386-5404.
- [47] R. Jin, Y. Liu, Z. Wu, H. Wang, T. Gu, Chemosphere. 78 (2010) 1160-1166.
- [48] W. Yao, X. Wang, Y. Liu, Z. Wu, Applied Surface Science. 467-468 (2019) 439-445.
- [49] G. Zhou, H. Liu, K. Cui, A. Jia, G. Hu, Z. Jiao, Y. Liu, X. Zhang, Applied Surface Science. 383

(2016) 248-252.

- [50] G. RAMIS, G. BUSCA, V. LORENZELLI, Materials Chemistry and Physics. 29 (1991) 425-435.
- [51] L. Zhang, H. He, Journal of Catalysis. 268 (2009) 18-25.
- [52] S.M. Lee, S.C. Hong, Applied Catalysis B: Environmental. 163 (2015) 30-39.
- [53] F. SOLYMOSI, T. BANSAGI, Journal of Catalysis. 156 (1995) 75-84.
- [54] H. He, C. Zhang, Y. Yu, Catalysis Today. 90 (2004) 191-197.
- [55] H.H. Ingelsten, R. Matarrese, M. Skoglundh, Topics in Catalysis. 52 (2009) 1921-1924.
- [56] M. Jabłońska, A. Król, E. Kukulska-Zajac, K. Tarach, L. Chmielarz, K. Góra-Marek, Journal of Catalysis. 316 (2014) 36-46.
- [57] K. Góra-Marek, K.A. Tarach, Z. Piwowarska, M. Łaniecki, L. Chmielarz, Catalysis Science & Technology. 6 (2016) 1651-1660.

**Fig. 1.** Light-off curves of CH<sub>3</sub>CN catalytic degradation over the CuCeO<sub>x</sub>-HZSM-5 composite catalysts: (a) CH<sub>3</sub>CN conversion; (b) CO<sub>2</sub> yield; (C) NO<sub>x</sub> yield; (d) NH<sub>3</sub>





**Fig. 2.** XRD patterns of the CuCeO<sub>x</sub>-HZSM-5 composite catalysts.



**Fig. 3.** H<sub>2</sub>-TPR profiles of the CuCeO<sub>*x*</sub>-HZSM-5 composite catalysts.

**Fig. 4.** XPS spectra of the CuCeO<sub>x</sub>-HZSM-5 composite catalysts: (a) CuCeO<sub>x</sub>; (b)



CuCeO<sub>x</sub>+HZSM-5; (c) CuCe/ZSM-5.

**Fig. 5.** CH<sub>3</sub>CN-TPSR profiles of the CuCeO<sub>x</sub>-HZSM-5 composite catalysts: (a)



CuCeO<sub>x</sub>; (b) CuCeO<sub>x</sub>+HZSM-5; (c) CuCe/ZSM-5; (d) HZSM-5.

#### Fig. 6. DRIFT spectra of HZSM-5 exposed to 600 ppm $CH_3CN+5\%$ O<sub>2</sub> for various



times at (a) 100, (b) 250, (c) 350 °C.

#### Fig. 7. DRIFT spectra of CuCeO<sub>x</sub> exposed to 600 ppm CH<sub>3</sub>CN+5% O<sub>2</sub> for various



times at (a) 100, (b) 250, (c) 350 °C.

Fig. 8. DRIFT spectra of (a) CuCeO<sub>x</sub>+HZSM-5 and (b) CuCe/ZSM-5 exposed to 600



ppm CH<sub>3</sub>CN+5% O<sub>2</sub> for various times at 250 °C.

### Fig. 9. Proposed mechanism of enhanced N<sub>2</sub> selectivity over CuCeO<sub>x</sub>-HZSM-5



composite catalysts.

Fig. 10. CH<sub>3</sub>CN conversion and NO<sub>x</sub> yield of CH<sub>3</sub>CN catalytic degradation over the

 $CuCeO_x + HZSM - 5 \text{ catalysts } (SiO_2/Al_2O_3 = 18, 27, 300). \text{ Conditions: } 600 \text{ ppm CH}_3CN, 5\% O_2.$ 



Catalysts	$S_{BET}$ ( $m^2\!/g$ )	Pore	Pore		
		diameter	volume	$Ce^{3+}/Ce^{4+}$	Oads/Olatt
		(nm)	(cm <sup>3</sup> /g)		
CuCeO <sub>x</sub>	41.3	7.3	0.08	0.172	0.411
HZSM-5	370.3	2.3	0.21	-	-
CuCe/ZSM-5	168.0	3.2	0.13	0.138	0.203
CuCeO <sub>x</sub> + HZSM-5	215.0	3.3	0.18	0.176	0.442

### Table 1. Physical properties and XPS results of the CuCeO<sub>x</sub>-HZSM-5 composite

catalysts.