Investigation on structure-activity relationship and reaction pathways of CuO/CeO_2 catalysts for NH_3 self-sustained combustion

Running Kang[1], Mingxia Yang[1,2], Zirui Zhang[1], Chenhang Zhang[1,3], Xiaokun Yi[1], Feng Bin[*1], Xiaolin Wei[1]

[1]*State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, PR China.*

[2] *School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China.*

[3] *Key Laboratory of Beijing on Regional Air Pollution Control, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, PR China*

** Corresponding author: binfeng@imech.ac.cn*

Significance and Relevance

Catalytic combustion of high concentration NH_3 to produce N_2 and H_2O is a promising method for carbon-free fuel utilization, but is rarely reported so far. The distinct structure-activity relationship by designing CuO/CeO_2 catalysts with different CeO_2 morphologies was clearly identified. We found that NH_3 self-sustained combustion can be realized at a low NH_3 lean-combustion limit (7.6%) over Cu/Ce-Sphere at the first time. The comprehensive reaction mechanism involving intermediates transformation and contribution of different active oxygen species were revealed. These results demonstrated the viability of environmentally friendly catalytic combustors for ammonia fuel, and advanced the understanding of ammonia catalytic reaction mechanism.

Preferred and 2nd choice for the topic: Air cleaning and combustion, Fundamental advances in understanding catalysis

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Introduction and Motivations

Ammonia (NH_3) as a promising carbon-free fuel has attracted massive attention that aim to promote carbon peak and carbon neutrality progress. It has advantages in carbon-free footprint, high energy density, and low storage and transportation costs. However, the challenges of NH_3 utilization are its high ignition temperature and poor combustion stability and higher content of NO_x emission during direct combustion process[1]. The catalytic combustion of NH_3 to produce nitrogen (N_2) and water (H_2O) is an innovative method to solve mentioned problems, attributed to its limited NO_x production at low operating temperature, and high activity with stable combustion [2]. Intensively studies of the catalytic ammonia oxidation have been performed to remove NH_3, in situation of NH_3 is regarded as air pollutant with a low concentration (≤1%)[3,4], rather than catalytic combustion for high concentration (~10%) of NH_3 fuel. And the transition metal oxides catalysts (CuO, CeO_2, etc.) have been accepted as an alternative to noble metals, due to their low cost, excellent activity and stability[5,6]. However, the structure-activity relationship over CuO–CeO_2 catalysts remain an unresolved problem.

Therefore, this study firstly identified the distinct structure-activity relationship by designing the CuO/CeO_2 catalysts with different morphologies of CeO_2. And the combustion characteristic of high concentration (~10%) of NH_3 including self-sustained combustion limit, conversion efficiency, the wall temperature, and stability were revealed. Specifically, the detailed reaction pathways were fully discussed. These results are beneficial to make an intensive understanding of distinct structure-activity relationship and comprehensive reaction mechanism over CuO/CeO_2 for catalytic NH_3 combustion.

Materials and Methods

The nano sphere CeO_2 (Ce-S), rod CeO_2 (Ce-R) and octahedral CeO_2 (Ce-O) carriers were synthesized through a hydrothermal synthesis method. Then different CuO/CeO_2 samples were prepared with an impregnation method and denoted as Cu/Ce-S, Cu/Ce-R, and Cu/Ce-O, respectively.

Results and Discussion

The reaction activity for NH_3 catalytic ignition decreases in the subsequence of Cu/Ce-S > Cu/Ce-R > Cu/Ce-O > Ce-S, corresponding to the T_{90} (the temperature at 90% NH_3 conversion) of 220 °C, 252 °C, 287 °C, and 411 °C, respectively (Fig.1a). Compared with activity and N_2 yield of Ce-S, that of other three catalysts markedly improved, indicating the addition of CuO exhibits stronger interaction of CuO and CeO_2 and promotes the conversion of ammonia to nitrogen (Fig.1b). It is clear that the Cu/Ce-S

exhibits the highest catalytic performance, attributed to a stronger structure-activity relationship, including sphere CeO_2 with higher SSA for CuO_x dispersion, more Cu-O_x-Ce solid solution with oxygen vacancy, and stronger reducibility and oxygen mobility, etc. The NH_3 lean-combustion limits of Cu/Ce-S is 7.6% to maintain self-sustained combustion (Fig.1c). And Cu/Ce-S exhibits a remarkable performance with high NH_3 conversion (~100%) and effective N_2 yield (~98.0 %) over 360 min (Fig.1d). Such superior activity of Cu/Ce-S is attributed to the robust interaction of CuO and Ce-S (111 and 220 planes) on the oxide phases interface, reflecting the higher SSA for CuO_x dispersion to adsorb ammonia, and more Cu-O_x-Ce solid solution with oxygen vacancy (Cu^+-O_V-Ce^{3+}) to promote the active oxygen formation and mobility. The reaction mechanism for NH_3 combustion over Cu/Ce-S is also proposed. The M-K mechanism is dominant, involving the adsorbed NH_x by ammonia dehydrogenation to react with active lattice oxygen to produce N_2 and H_2O. And the L-H mechanism plays a subordinate contribution due to the formation of adsorbed HNO species. The additional *i*-SCR reaction can effectively reduce the NO formation.

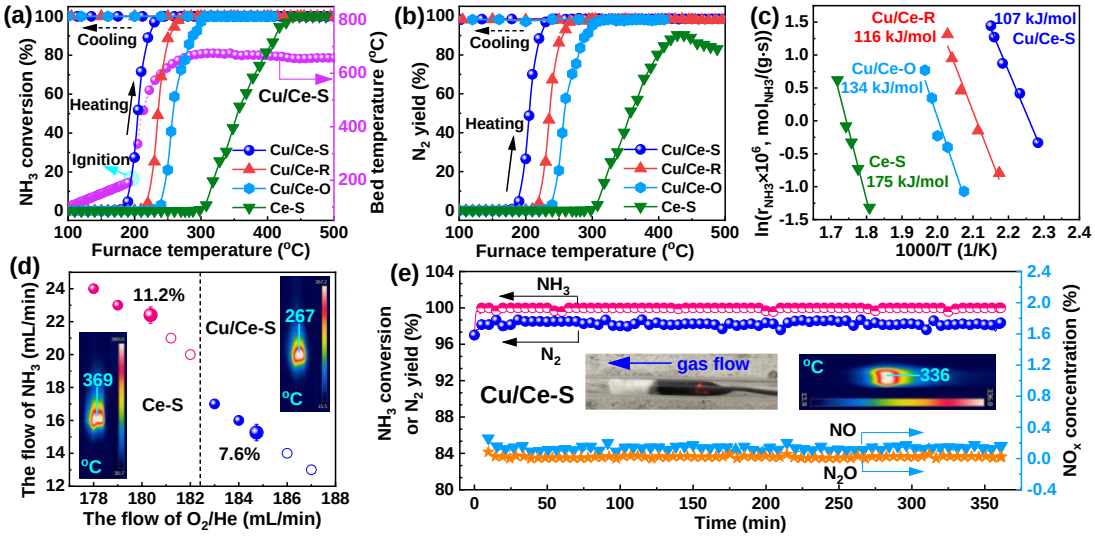

Figure 1 NH_3 conversion (a), N_2 yield (b), Arrhenius curves (c) of catalysts, lean-combustion limits (d), and stability (e) results of Cu/Ce-S under 10% NH_3+21% O_2/Ar.

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