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EFFECT OF NF₃ GAS ON STABILIZATION OF ALKALINE EARTH METAL-Cu MORDENITE CATALYSTS DURING N₂O DECOMPOSITION REACTION

Mordenite-zeolite supported Ca-Cu and Ba-Cu catalysts (Ca-Cu/MOR and Ba-Cu MOR) were successfully fabricated for direct decomposition of both NF₃ and N₂O gases contained in waste gas stream of (semiconductor) electronics industry. N₂O conversion rates of Ca-Cu and Ba-Cu catalysts were 79 and 86%, respectively, at 700°C and 1 atm under space velocity of 5000 h⁻¹. The Ca-Cu catalyst was especially noteworthy in that its capability of converting N₂O could be maintained even after its exposure to co-feeding NF₃ gas constituent in the waste gas stream. Compositional and surface morphological analyses of the Ca-Cu and Ba-Cu catalysts were made before and after exposure to the waste gas stream to examine any noticeable degradation or change of the catalysts. Unlike Ba-Cu catalyst, SiO₂ constituent of the Ca-Cu catalyst was found to remain immune to the NF₃-cofeeding waste gas stream, casting a positive prospect for superior and steady N₂O decomposition performance via maintenance of its structural integrity.

Keywords: nitrous oxide (N₂O), nitrofluorine three (NF₃), perfluorocompounds (PFCs), direct decomposition, catalyst

1. Introduction

Non-CO₂ greenhouse gases (CH₄, SF₆, NF₆, N₂O) are extensively used for etching and evaporation of insulating layers in semiconductor and display manufacturing processes at ever increasing rate. Perfluorocompounds (PFCs) and nitrous oxide (N₂O) gas need to be effectively removed and abated for high global warming potential mainly caused by their long residence time in the atmosphere. Diverse research is thus underway to develop efficient method of decomposition and conversion of these gases [1-3].

Nitrous oxide (N₂O) is an important reactant gas for use in semiconductor industry to evaporate SiO₂ layer via the reaction: $\text{SiH}_4 + 2 \text{N}_2\text{O} \rightarrow \text{SiO}_2 + 2 \text{N}_2 + 2 \text{H}_2$

SiO₂ is an indispensable insulating layer over the silicon wafer during fabrication of dynamic random access memory (DRAM), flash random access memory (RAM) and large scale integration (LSI) logic chip. N₂O gas is also extensively utilized in other industrial sectors at increasing rate [4-5]. Direct decomposition, thermal decomposition and selective catalytic reduction are mainly used for conversion of N₂O and operational environment has usually dictated optimization of N₂O removal technology in terms of outgoing N₂O concentration and temperature [6-9]. However, a dearth of literature has been

found on the effect of PFCs on structural integrity of catalysts for removal and abatement of nitrous oxide (N₂O) under co-feeding perfluorocompounds (PFCs) in the gas stream.

Nowadays, various technologies are used to decompose PFCs such as plasma, direct combustion, indirect heating, and catalytic conversion [10-12]. The PFC-emitting source industries select one of these technologies based on the condition and environment of operation as well as specificity of the gaseous PFC exhaust and the ensuing suitability of the technology. More specifically, plasma decomposition technology is highly efficient but costly in operation and generates voluminous amount of by-products. On the other hand, direct combustion is the most readily accessible technology but production of thermal NO_x in large quantities is its downside. Decomposition of PFCs by indirect heating is an economical means for efficient decomposition of NF₃ and it has an advantage of possible addition of high temperature catalyst. Therefore, effective removal and abatement of N₂O gas was deemed technically feasible should structural integrity of the candidate catalyst be maintained under co-feeding of NF₃ in the waste gas stream.

Structural integrity of the catalyst when exposed to NF₃ gas is quite an indispensable factor as well as its capability to remove and abate N₂O. Therefore, effect of high NF₃ partial pressure in the waste gas stream on the catalyst performance was com-

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prehensibly investigated in the present paper. Most importantly, structurally stable catalyst composition was optimized with primary emphasis placed on its removal and abatement efficiency of N_2O gas with partial pressure variation of NF_3 in the co-feeding waste gas stream. The target application of the catalyst is in the aft portion of the semiconductor fabrication process.

2. Experimental

2.1. Catalyst Preparation

Catalyst was prepared based on Cu and mordenite zeolite (CBV21A from Zeolyst Co. Ltd.) and 5 wt. % of Ca or Ba was impregnated to fabricate co-catalyst of Ca-Cu (CCM) and Ba-Cu (BCM), respectively. More specifically, the catalysts were wet-impregnated at $80^\circ C$, dried at $110^\circ C$ under ambient air for 24 h before being calcined in air for 4 h at $800^\circ C$ with $10^\circ C/min$ heating rate. Experimental procedure for preparation of the catalysts is shown in Figure 1. As for preparation of Ba-Cu (BCM) catalyst, proper amount of $Ba(NO_3)_2 \cdot 4H_2O$ was added instead of $CaCl_2 \cdot H_2O$ for wet impregnation at $80^\circ C$. All in all, 5 wt.% of either Cu or Ba was impregnated: 1.5 g of either Ca or Ba along with 14.25 g of Cu and 14.25 g of mordenite support, following the procedure of Figure 1.

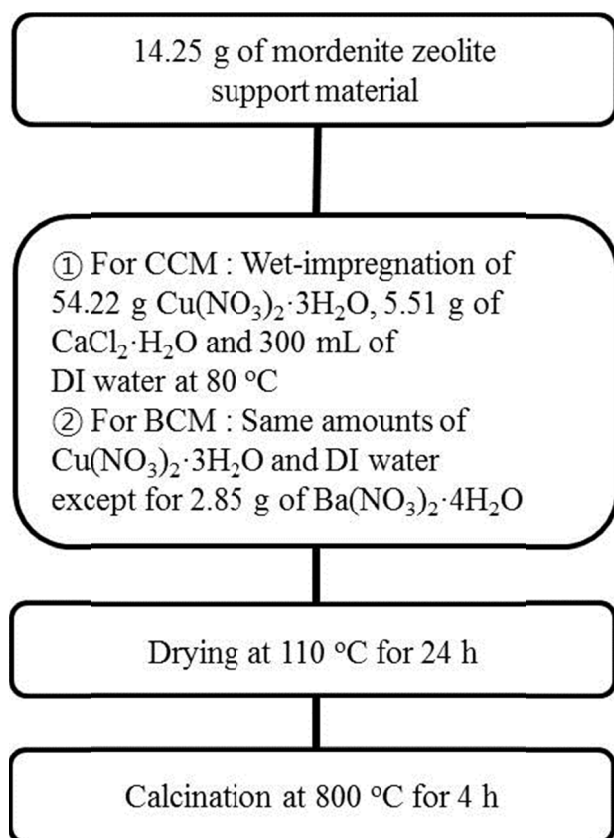


Fig. 1. Detailed flow diagram for preparation of DeN_2O catalysts: 54.22 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 5.51 g of $CaCl_2 \cdot H_2O$ contain 14.25 g of Cu and 1.5 g of Ca, respectively. On the other hand, 54.22 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 2.85 g of $Ba(NO_3)_2 \cdot 4H_2O$ contain 14.25 g of Cu and 1.5 g of Ba, respectively

2.2. Catalyst Characterization

For catalytic activity test, N_2O decomposition experiments were conducted on a fixed bed flow reactor at $700^\circ C$ under ambient atmosphere with N_2O concentration of 3,000 ppm and controlled space velocity of $5000 h^{-1}$. To investigate into the effect of NF_3 concentration, its partial pressure was varied as described in the Table 1. X-ray fluorescence (XRF) was used for quantitative surface elemental analysis while the specific surface area was measured by N_2 adsorption/desorption isotherms using XRF-1800 of Shimadzu Corp. Japan and Brunauer-Emmett-Teller (BET) analyzer (Tristar II 3020 of Micromeritics Instrument Corp. USA). Finally, concentrations of N_2O and NF_3 in the waste gas stream were measured at real time basis using Fourier-transform infrared spectroscopy (IG-2000 of Otsuka Electronics Co., Ltd. Japan) for evaluation of catalyst conversion efficiency.

TABLE 1

Experimental conditions for N_2O decomposition reaction: GHSV represent gas hourly space velocity

Variables		Values
Temperature ($^\circ C$)		700
GHSV (h^{-1})		5,000
Concentrations of Reactant gases (ppm)	N_2O	3,000
	NF_3	3,000, 6,000, 12,000
	N_2	balance

3. Results and discussion

Firstly, N_2O conversion rates were examined under sole presence of N_2O at 3,000 ppm in the gas stream as described in the third row from the bottom of Table 1. The result is shown in Figure 2a where catalytic activities of Ca-Cu (calcium-copper-mordenite, CCM) and Ba-Cu (barium-copper-mordenite, BCM) are 79.3 and 86.2%, respectively, during their exposure to N_2O gas stream for 10 h. Effect of NF_3 co-feeding on the catalytic activities is depicted in Figure 2b. While BCM catalyst showed excellent catalytic activity under sole N_2O in the gas stream, it was inferior to CCM catalyst under co-feeding of NF_3 . BCM catalytic activity drastically decreased with NF_3 concentration in the range of 3000-12000 ppm. In contrast, catalytic activity of CCM catalyst is especially noteworthy in that N_2O conversion rate of 50% was obtained after 30 min under 12000 ppm of NF_3 co-feeding as overlaid in Figure 2b, showing some positive prospect in maintaining adequate level of catalytic activity with co-feeding of NF_3 . Variation of BCM catalytic activity with time is appended in Figure 2c, where catalytic conversion rate of 45% was observed after 30 min exposure to co-feeding of NF_3 at 6,000 ppm and 3,000 ppm of N_2O . The squares on top of the Figure 2b represent conversion efficiency of NF_3 gas under co-feeding environment and it was completely decomposed by both BCM and CCM catalysts.

All data points in Figure 2b were obtained after ~1h exposure to the co-feeding gas stream.

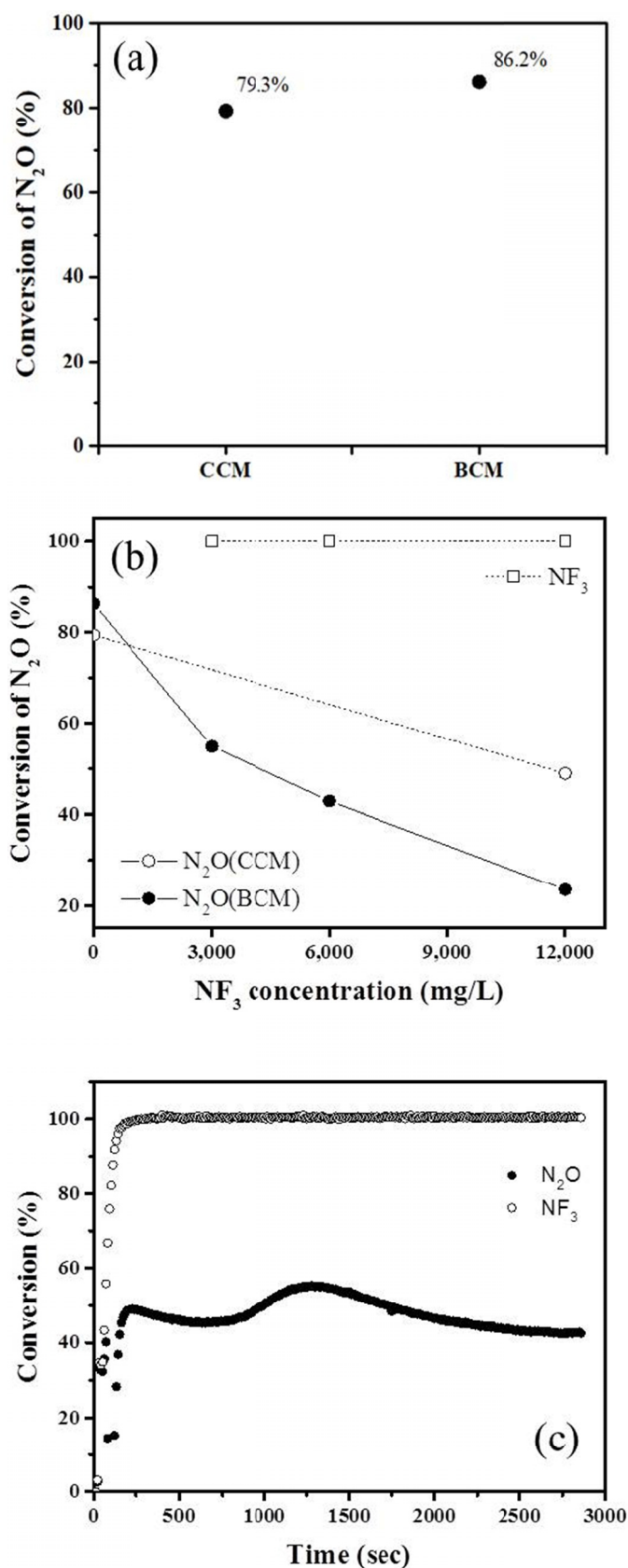


Fig. 2. Catalytic activities for N₂O decomposition, a) Effect of catalyst, b) Effect of NF₃ concentration, c) Conversion rates of N₂O and NF₃ gas with time for the BCM catalyst under co-feeding of N₂O and NF₃ at 3,000 ppm and 6,000 ppm, respectively

Quantitative analysis on catalysts composition was performed by using XRF and the results shown in wt. % in Table 2. CCM catalyst displayed very little compositional change but BCM catalyst lost significant portion of its original SiO₂ contents. This is attributed to structural distortion and consequent degradation of catalytic activity of BCM catalyst caused by exposure to NF₃ gas although its catalytic activity is quite excellent under sole presence of N₂O in the gas stream. Slow decline of catalytic activity with time as manifested in Figure 2c is attributed to some structural degradation. TEM micrographs of Figure 3 were taken in support of XRF and BET analyses results of Table 2. Unlike CCM catalyst, significant morphology change by agglomeration of surface pores was observed for BCM catalyst after 10 h exposure to co-feeding environment, which is attributable to decline of (surface) catalytic activity of BCM catalyst. More specifically, (catalytically active) surface pores on CCM catalysts ranged from 60 to 80 nm sizes with no apparently accompanying surface morphology change before and after exposure to co-feeding environment, which was also hinted by XRF analysis.

Previous XRF analysis of spent BCM catalyst revealed reduction of surface SiO₂ contents and BET specific surface area. The average surface catalytic pore size on BCM catalyst was 30 nm, which was relatively smaller than that of CCM catalyst. Moreover, average size of Ba surface catalysts increased from 3–4 nm to 10 nm, cogently substantiating sintering process. Therefore, the observed sintering reaction, combined with significant loss of SiO₂ constituent as manifested by XRF analysis result, synergistically contributed to irreversible loss of surface catalytic sites caused by structural degradation of mordenite support.

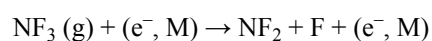
Contrary to expectations, Cl⁻ was not detected by XRF method on CCM surface and it is attributed to loss of significant portion of it during CCM catalyst preparation as detailed in Figure 1. Although further supplementary research is to be warranted for investigation into the possible role of Cl⁻ contents on better performance of CCM catalyst in the co-feeding gas stream, it is strongly inferred from the TEM micrographs of Figures 3c and d that Cl⁻ contents proprietarily added to CCM catalyst is related to beneficial effect of Cl⁻ contents on surface catalytically active sites.

As for mechanisms for catalytic conversion of NF₃ and N₂O, mechanistic experiments were not performed in the present research but previous literature were comprehensively reviewed [13–18], where various intermediate reaction mechanisms were suggested for different experimental apparatus, procedure and environment.

Takubo et al. [13] suggested NF₃ decomposition mechanism under humid gas environment at 450–600 K on metal phosphates:



However, the following mechanisms seem to be more plausible for dry gas atmosphere without oxygen in the present experiment [14–16]:



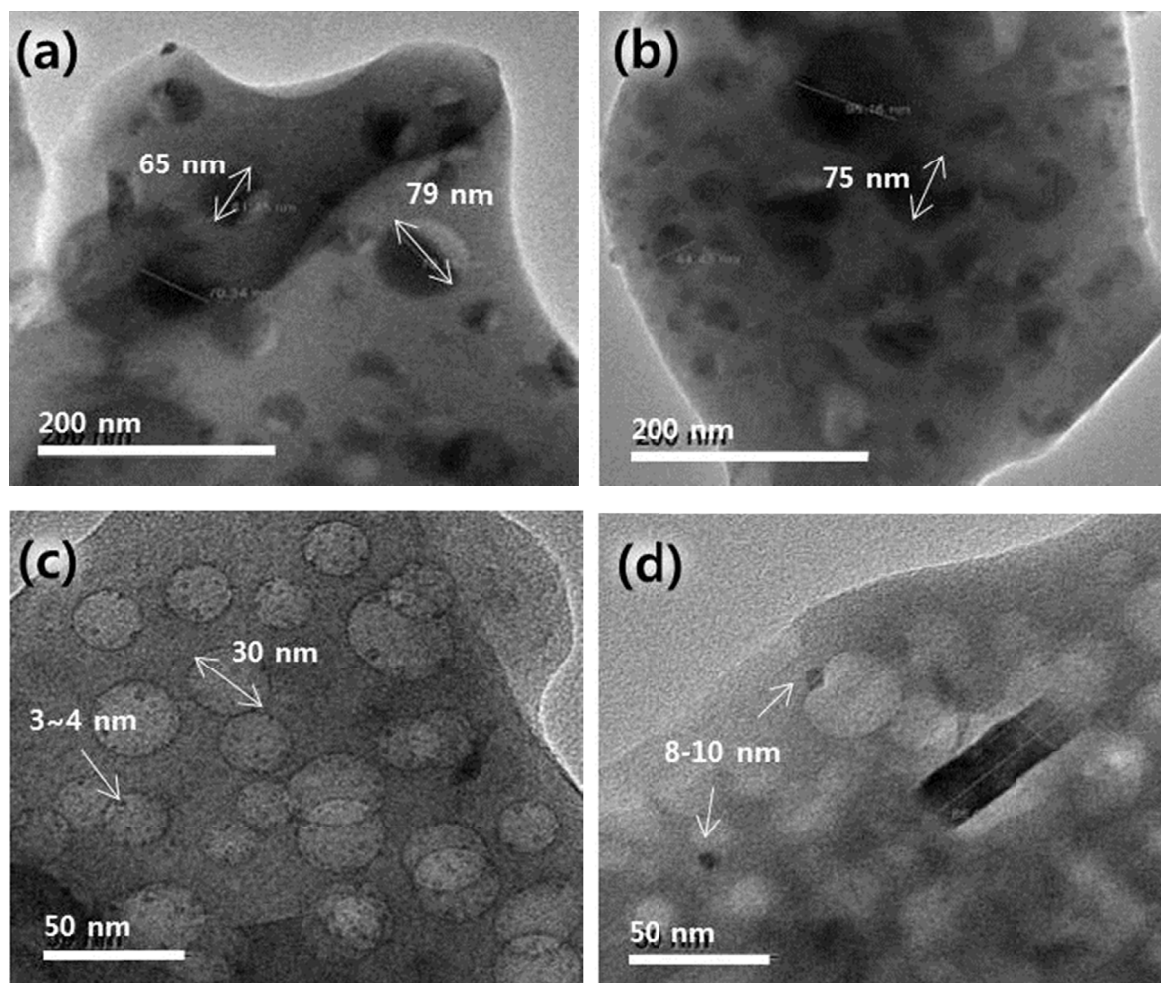
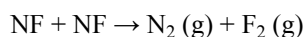
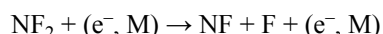
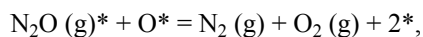
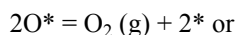
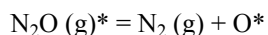
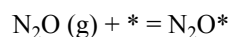


Fig. 3. TEM micrographs of surface morphology before and after 10 h exposure to co-feeding gas stream of NF_3 and N_2O at 12,000 and 3,000 ppm, respectively. CCM catalysts before and after exposure are depicted in (a) and (b), respectively. Pre- and post-exposure surface morphology of BCM catalysts are also shown in (c) and (d), respectively



(e^-, M) represents electrons on the catalytically active material, M.

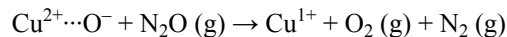
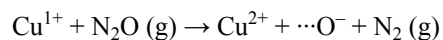
Mechanisms for N_2O conversion have also been extensively surveyed [17-18]. Dandekar and Vannice [17] suggested reaction intermediates involving adsorption of N_2O , subsequent decomposition into adsorbed atomic oxygen on the catalytically active sites of Cu/ZSM-5 and $\text{Cu/Al}_2\text{O}_3$ at 500°C before final formation of $\text{O}_2 (\text{g})$ and active sites:



where $*$ and O^* represent catalytic surface active sites and active oxygen species, respectively.

On the other hand, more reasonably comparable example was studied by Campa et al. [18] who fabricated and character-

ized Cu-Na-MOR catalyst where catalytic decomposition of $\text{N}_2\text{O} (\text{g})$ at 500°C is explained by oxidation number of copper and reaction intermediate of adsorbed O^- radical:



Secondly, effects of stepwise sequential compositional variation in the gas stream on the catalytic activity were investigated. In Figure 4, 1st, 2nd, and 3rd steps are explained in the legend box along with N_2O decomposition efficiency of CCM and BCM catalyst in terms of bar graphs representing numerical conversion rates. 2 sets of 3 sequential experiments generated N_2O conversion rates in terms of percent(s) numerically written inside of the bar graphs. For each set of 3 experiments, same catalyst was used throughout. Contrary to BCM catalyst, N_2O removal efficiency of CCM catalyst recovered to its pre- NF_3 exposure level once NF_3 flow was cut off. This indicates possible repeatability of CCM catalyst by maintaining its structural integrity and surface regeneration. Compositional analyses of the BCM and CCM catalysts were thus made to experimentally substantiate the observed behavior.

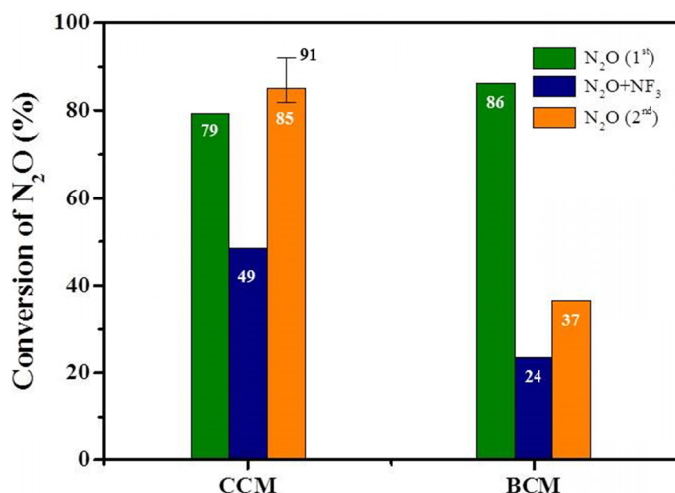


Fig. 4. Effects of stepwise sequential compositional variation in the gas stream on the catalytic activities for N₂O decomposition: error bar size in the third bar graph ranges from 85 to 91%. For each set of 3 experiments, same catalyst was used throughout

TABLE 2

Quantitative analysis on catalyst composition by using X-ray fluorescence (XRF) and Brunauer-Emmett-Teller (BET) analyzer. “Fresh” and “Spent” designate before and after exposure to the waste gas stream, respectively

Composition of catalysts		CuO	CaO	BaO	SiO ₂	Al ₂ O ₃	BET (m ² /g)
CCM	Fresh	64.1	8.0	-	26.2	1.5	2.1
	Spent	65.9	7.0	-	23.9	1.5	2.3
BCM	Fresh	57.3	-	5.9	34.6	2.0	4.2
	spent	75.5	-	5.9	15.5	1.7	4.1

4. Summary

Cu mordenite-supported alkaline earth metal-catalysts of Ba-Cu/MOR (BCM) and Ca-Cu/MOR (CCM) were fabricated to investigate into their N₂O decomposition characteristics under high concentration of NF₃ co-feeding in the N₂O-containing gas stream. Under sole presence of N₂O in the gas stream, N₂O conversion rates of CCM and BCM catalysts at 700°C were 79.3 and 86.3%, respectively. However, co-feeding of NF₃ to the gas stream changed N₂O conversion rates to 49 and 24% for CCM and BCM catalysts, respectively, which is contrary to their catalytic behavior displayed during their exposure to sole N₂O atmosphere. Furthermore, XRF analysis results confirmed very little compositional change of CCM catalyst after its exposure to NF₃ atmosphere but considerable reduction of SiO₂ contents of the BCM catalyst was deemed responsible for its consequent structural distortion. The lower N₂O conversion efficiency of CCM catalyst under mixed atmosphere of NF₃ and N₂O than its performance under sole N₂O atmosphere is attributed to surface competitive reaction between N₂O and NF₃. However,

compositional and structural integrity was maintained after CCM catalyst's exposure to high concentration of co-feeding NF₃, which casts a very positive prospect of CCM catalyst for catalytic removal and abatement of both NF₃ and N₂O under co-feeding environment at 700°C, usually encountered in the aft portion of semiconductor fabrication industry.

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