

## CuO supported on CeO<sub>2</sub> materials as catalysts for degradation of N<sub>2</sub>O emissions

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### Introduction

Over the past decades, nitrous oxide (N<sub>2</sub>O) has been considered as an environmental pollutant because it is a strong greenhouse gas, which global warming potential is 310 times higher as compared to carbon dioxide [1]. Furthermore, nitrous oxide is responsible for destruction of ozone in the stratosphere and has a very long atmospheric lifetime (approx. 120 years). Up to date, different types of catalysts have been investigated in catalytic N<sub>2</sub>O degradation. Among them, Cu-based materials have a great advantage because of low cost and excellent catalytic performance. Here we report a new, highly active CuO/CeO<sub>2</sub> catalyst for low temperature N<sub>2</sub>O decomposition. The present work was aimed to correlate Cu loading, presence of small CuO clusters, active sites (Cu<sup>+</sup>) determined by TPR/UV-Vis/*in situ* DRIFTS and catalytic activity of CuO-CeO<sub>2</sub> catalysts.

### Materials and Methods

Nanosized CeO<sub>2</sub> support was prepared using glycothermal approach. The molar gel composition and utilized time during the glycothermal synthesis were 1 Ce(NO<sub>3</sub>)<sub>3</sub> : 5.5 CH<sub>3</sub>CH<sub>2</sub>COOH : 220 HOCH<sub>2</sub>CH<sub>2</sub>OH and 200 min, correspondingly. Synthesis temperature was varied from 140 to 160 °C. Product was centrifuged, dried overnight and calcined at 400 °C. CuO (5-20 wt. %) was deposited using wet impregnation (IMP) with aqueous Cu(NO<sub>3</sub>)<sub>2</sub> or pH controlled precipitation of Cu(OH)<sub>2</sub> by ammonia (CP) methods (Table 1). Prepared materials were characterized by BET, SEM, TEM, XRD, H<sub>2</sub>-TPR, *in situ* FTIR and UV-Vis techniques. Catalytic activity was investigated in a fixed-bed reactor operating in the temperature range from 300 to 550 °C with N<sub>2</sub>O feed concentration of 2500 ppm by volume.

### Results and Discussion

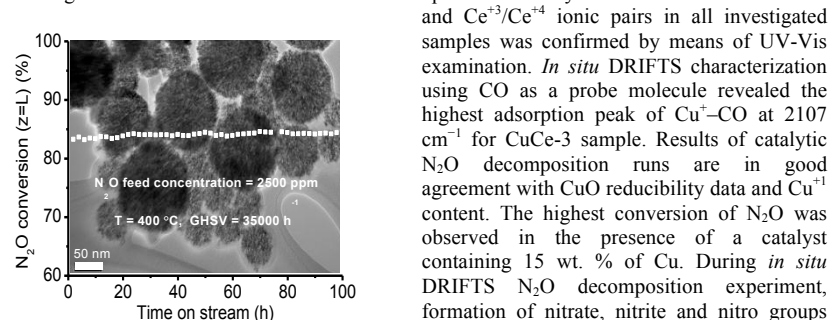
Different glycothermal treatment temperatures greatly influence the properties of the prepared CeO<sub>2</sub> supports. Increasing temperature from 140 to 160 °C during CeO<sub>2</sub> synthesis protocol results in higher BET specific surface area. However, further increase of hydrothermal treatment temperature leads to particle aggregation and decrease of BET specific surface area as well as catalytic activity during N<sub>2</sub>O degradation. For this reason, CeO<sub>2</sub> support prepared at 160 °C was further utilized.

XRD patterns for CuCe-1 – CuCe-4 materials importantly show formation of segregated CuO phase (characteristic peaks at 35.49 and 38.73° belonging to monoclinic CuO phase) for samples with Cu loading higher than 15 wt. %. Results of H<sub>2</sub>-TPR experiments revealed strong interactions between CuO and CeO<sub>2</sub> oxide phases and lower reduction temperatures in comparison with individual CuO and CeO<sub>2</sub> oxides, respectively. Several reduction peaks were observed, which can be attributed to the reduction of finely dispersed CuO with strong interaction with CeO<sub>2</sub>, small CuO clusters, reduction of larger CuO particles

**Table 1.** Physicochemical and catalytic properties of prepared CuO-CeO<sub>2</sub> materials.

Sample	w(Cu) (%)	Preparation method	S <sub>BET</sub> (m <sup>2</sup> /g)	d <sub>CeO<sub>2</sub>, 111</sub> (nm)	d <sub>CuO, 111</sub> (nm)	X(N <sub>2</sub> O) at 400 °C and GHSV = 45000 h <sup>-1</sup> (%)
CuCe-1	5	IMP	160		-	38
CuCe-2	10	IMP	154		-	54
CuCe-3	15	IMP	141	6.2	17	60
CuCe-4	20	IMP	133		41	58
CuCe-5	15	CP	135		10	66

weakly associated with CeO<sub>2</sub> and partial reduction of CeO<sub>2</sub>. Accordingly to the TPR profiles, CuCe-3 solid possessed the highest content of small CuO clusters, while further increase of Cu loading leads to the formation of bulk CuO with poor reducibility. Existence of both Cu<sup>+/Cu</sup><sup>2+</sup>



**Figure 1.** N<sub>2</sub>O conversion measured at 400 °C as a function of time on stream and TEM image for CuCe-5 sample.

and Ce<sup>3+/Ce</sup><sup>4+</sup> ionic pairs in all investigated samples was confirmed by means of UV-Vis examination. *In situ* DRIFTS characterization using CO as a probe molecule revealed the highest adsorption peak of Cu<sup>+</sup>-CO at 2107 cm<sup>-1</sup> for CuCe-3 sample. Results of catalytic N<sub>2</sub>O decomposition runs are in good agreement with CuO reducibility data and Cu<sup>+</sup> content. The highest conversion of N<sub>2</sub>O was observed in the presence of a catalyst containing 15 wt. % of Cu. During *in situ* DRIFTS N<sub>2</sub>O decomposition experiment, formation of nitrate, nitrite and nitro groups were not observed. In order to further improve catalytic properties, we attempted to increase the content of highly active nano CuO clusters by using CP preparation approach. The synthesized CuCe-5 material showed higher CuO dispersion (accordingly to XRD and TEM examinations) and exhibited enhanced redox as well as catalytic properties in comparison with other samples. Long-term stability test of 100 hours (Figure 1) confirmed excellent catalytic stability of the investigated CuCe-5 sample, which can be attributed to its ability to regenerate active sites by desorption of formed oxygen from the catalyst surface, as evidenced by an alternating N<sub>2</sub>O/N<sub>2</sub> TG experiment.

### Significance

Formation of segregated CuO phase negatively impacts reducibility and activity of CuO/CeO<sub>2</sub> catalysts for N<sub>2</sub>O degradation. Using controlled precipitation technique it was possible to considerably increase CuO dispersion, redox properties and catalytic activity. CuCe-5 catalyst exhibited good catalytic stability, which was confirmed by long-term stability tests performed in the period of 100 h.

### Reference

1. <http://epa.gov/climatechange/ghgemissions/gases/n2o.html>, accessed 13.01.2014.