Supporting information

# Ammonia formation by reduction of nitrogen monoxide with carbon monoxide using copper-deposited ceria in the presence of water

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## Catalyst preparation

Copper catalysts were prepared using the incipient wetness approach. $CeO_2$ (Type A, Daiichi Kigenso Kagaku Kogyo Co., Ltd.), $TiO_2$ (SSP-M, Sakai Chemical Industry Co., Ltd.), $Al_2O_3$ (Kojundo Chemical Lab. Co., Ltd.), $ZrO_2$ (RSC-H, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) and $SiO_2$ (Q-15, Fiji Silysia Chemical Ltd.) were employed as a support, and $Cu(NO_3)_2$ (FUJIFILM Wako Pure Chemical Corporation) was employed as a Cu precursor. The sample was calcined at 773 K for 4 h after 1 wt%, 3 wt%, 5 wt%, 10 wt%, 20 wt%, and 40 wt% Cu loading, and then reduced under 10 vol%$H_2/N_2$ at 673 K for 1 h.

## Catalytic reaction

A catalytic activity test was conducted employing a fixed bed flow reactor. The sample used was 0.15 g. The concentration of NO-CO-$H_2O$ reaction was 1000 ppm NO, 3000 ppm CO, and 1% $H_2O$. Feed gas compositions of WGS reaction, NO-$H_2$ reaction, and NO-CO reaction were 3000 ppm CO and 1% $H_2O$, 1000 ppm NO and 3000 ppm $H_2$, and 1000 ppm NO and 3000 ppm CO with balance Ar, respectively. Product analysis was conducted in the same manner as previously stated.[1]

## Defuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

During the NO-CO-$H_2O$ reaction, DRIFTS was performed to observe surface intermediate species. An FT-IR (iS50 FT-IR, Thermo Fisher Scientific) equipped with a DRIFT cell (1000 °C Heat Chamber, ST Japan Inc.) was employed. Pretreatment was conducted under 10 vol% $H_2$ with balanced Ar at 673 K for 0.5 h, and then measurement was performed under 1000 ppm NO, 3000 ppm CO, and 0.5% $H_2O$ at 423 K. The total gas flow was 30 mL/min.

1. K. Kobayashi, R. Atsumi, Y. Manaka, H. Matsumoto and T. Nanba, *Catal. Sci. Technol.*, 2019, **9**, 2898.

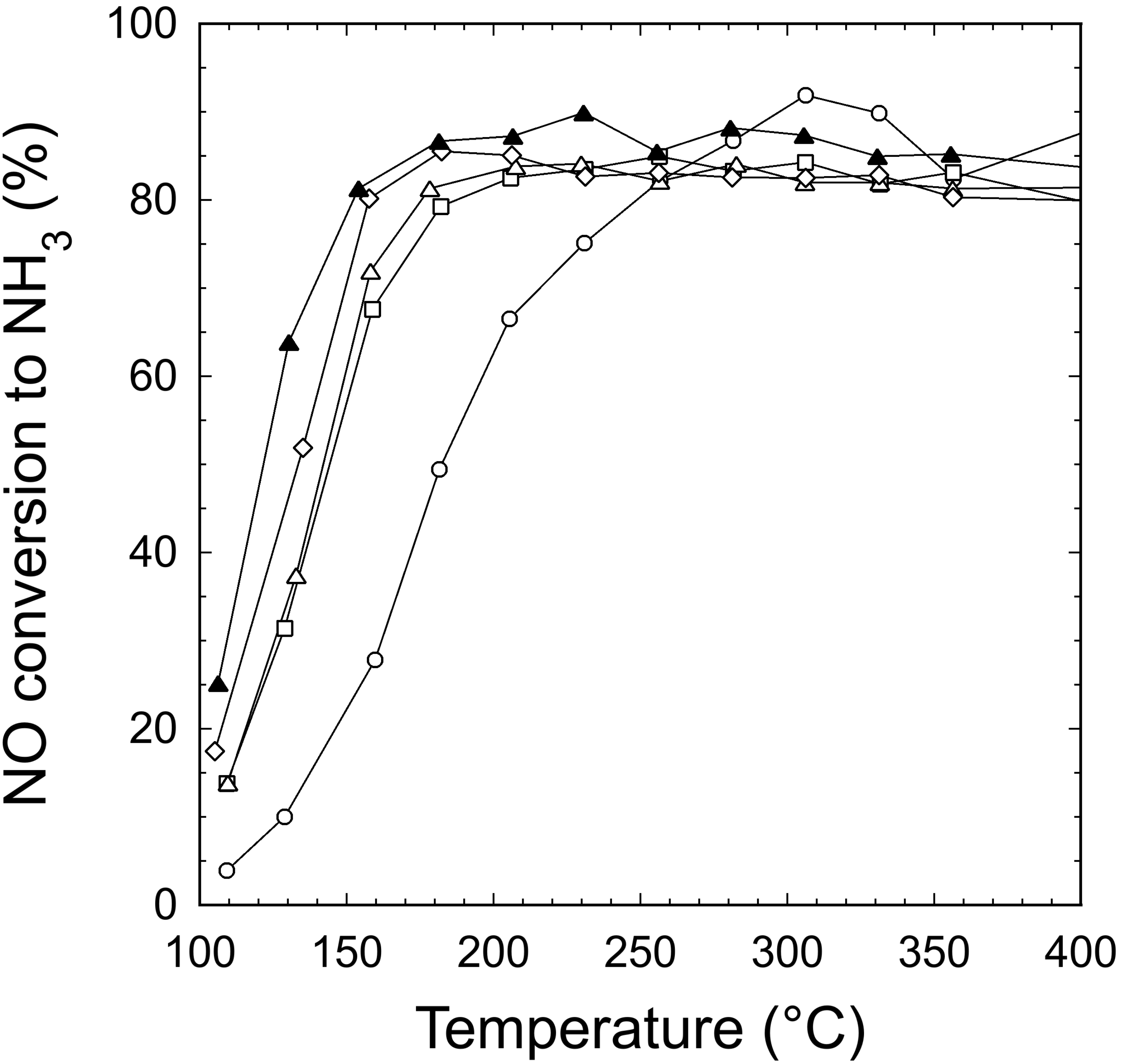

**Fig. S1.** NO conversion to $NH_3$ of X wt% Cu/$CeO_2$ catalysts (X = 1 wt%(open circle), 3 wt%(open square), 5 wt%(open triangle), 10 wt%(open diamond), 20 wt%(filled triangle), 40 wt% (filled diamond)) under NO-CO-$H_2O$ reaction

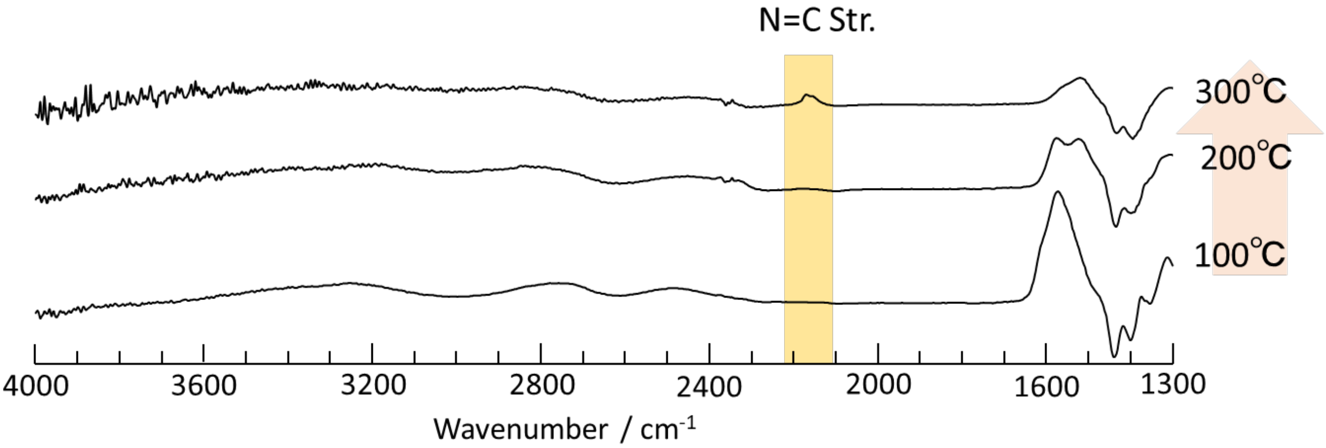

**Fig. S2.** Infrared spectra of the catalyst surface when NO and formic acid are adsorbed on the catalyst at room temperature and then the temperature is increased

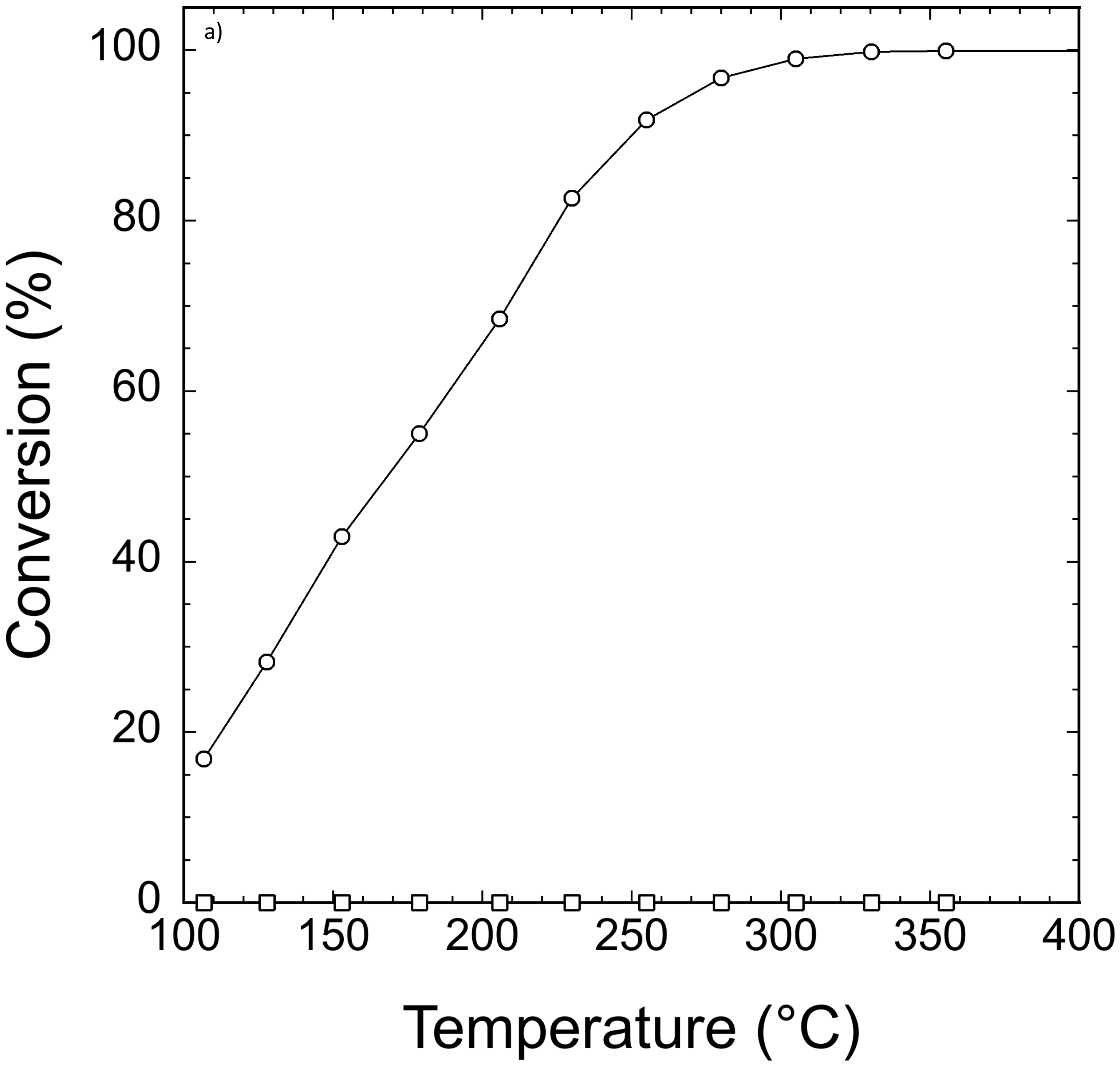

**Fig. S3a.** Catalytic activity of $Cu/CeO_2$ under NO-CO. a) NO conversion (open circle), and NO conversion to $NH_3$(open square)

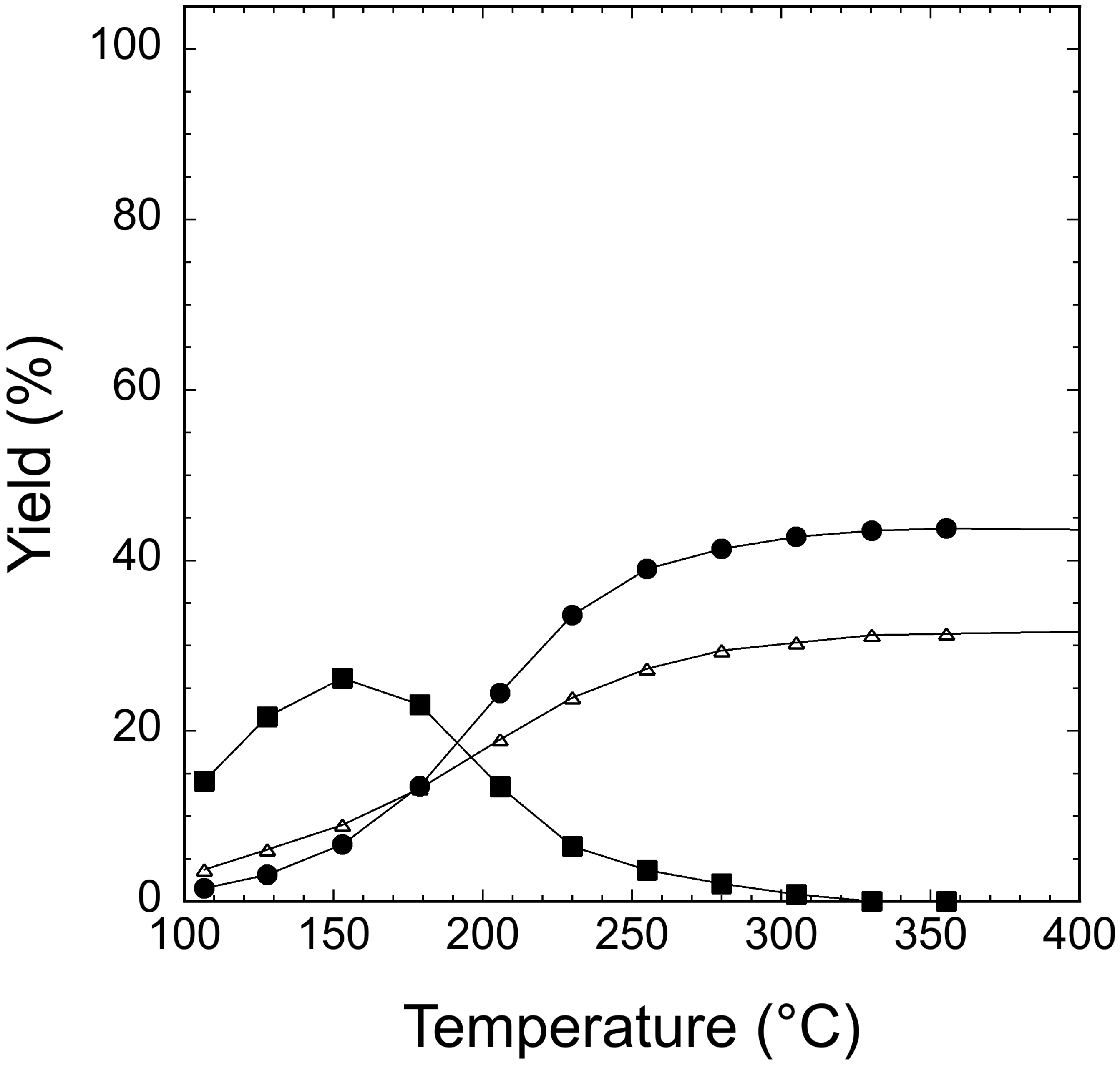

**Fig. S3b.** Catalytic activity of Cu/CeO$_2$ under NO-CO. b) N$_2$ yield (filled circle), N$_2$O yield (filled square) and CO yield (open triangle)

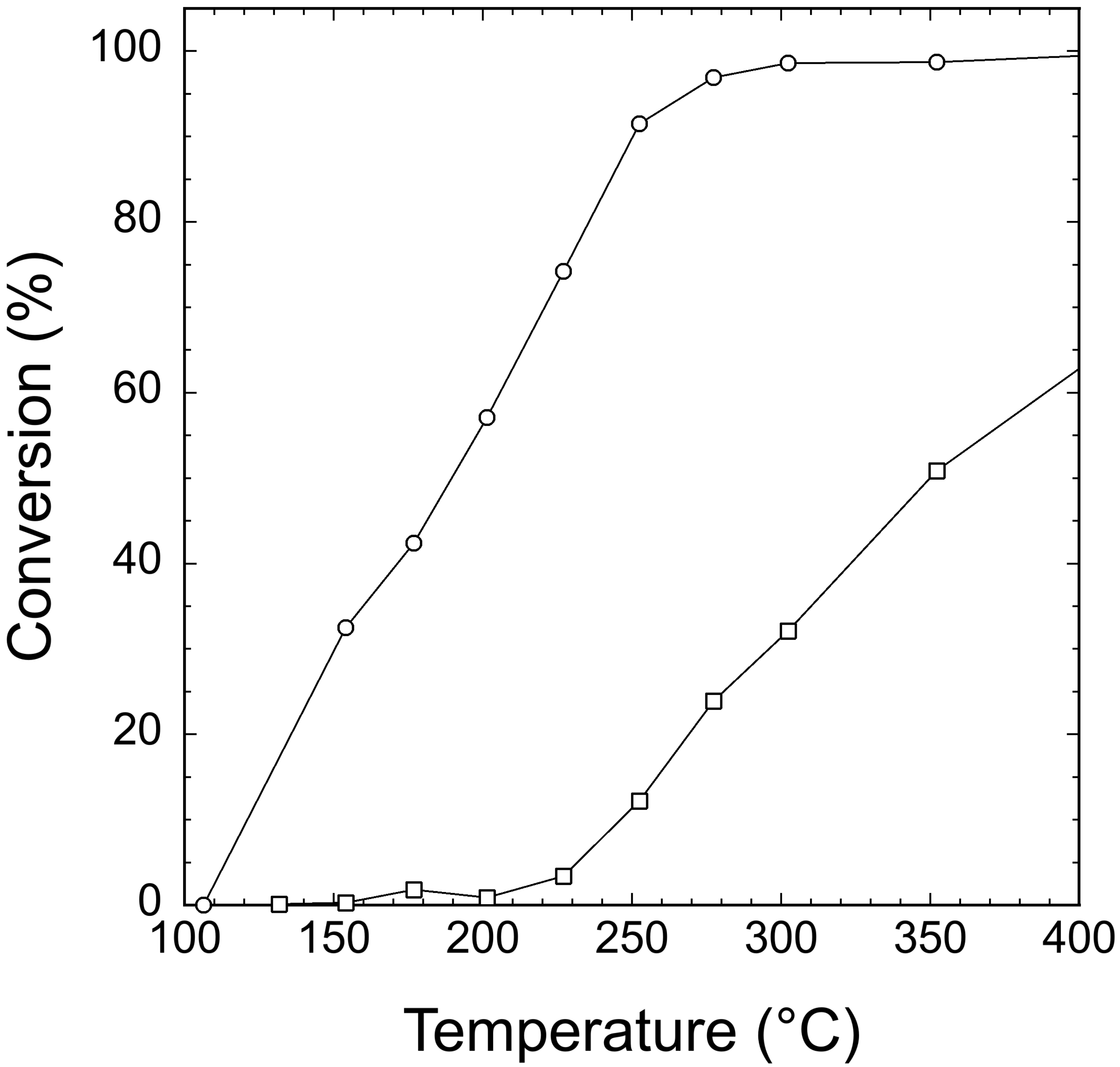

**Fig. S4.** Catalytic activity of Cu/$CeO_2$ under NO-CO-$H_2$. a) NO conversion (open circle), and NO conversion to $NH_3$(open square)