## NH<sub>3</sub> formation pathways from NO reduction by CO in the presence of water over Rh/Al<sub>2</sub>O<sub>3</sub>

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Steady-state kinetic measurements with varying NO (0.05–0.2 kPa), CO (0.2–0.5 kPa), and water (1.5–9 kPa) pressures at 598 K rationalize that  $N_2/N_2O$  selectivity is determined by NO pressure while the NH<sub>3</sub>/(N<sub>2</sub>O + N<sub>2</sub>) selectivity is a single-valued function of NO/CO ratio. The existence of NCO\* species on Al<sub>2</sub>O<sub>3</sub> is confirmed by IR spectra. Monotonically increasing NH<sub>3</sub>/Rh ratios from H<sub>2</sub>O recirculation over the NCO\* accrued in transient reaction studies on Rh/Al<sub>2</sub>O<sub>3</sub> upon exposure to NO/CO mixtures suggests NH<sub>3</sub> formation occurs by hydrolysis of isocyanate species bound on Al<sub>2</sub>O<sub>3</sub>. These findings demonstrate the critical role of H<sub>2</sub>O and NO/CO ratio in determining NH<sub>3</sub> selectivity for the operation of three–way automotive exhaust catalysts at rich air/fuel ratios.