

Supporting Information

$\text{MeO}_x/\text{Al}_2\text{O}_3$ and $\text{MeO}_x/\text{CeO}_2$ (Me = Fe, Co, Ni) catalysts for high temperature N_2O decomposition and NH_3 oxidation

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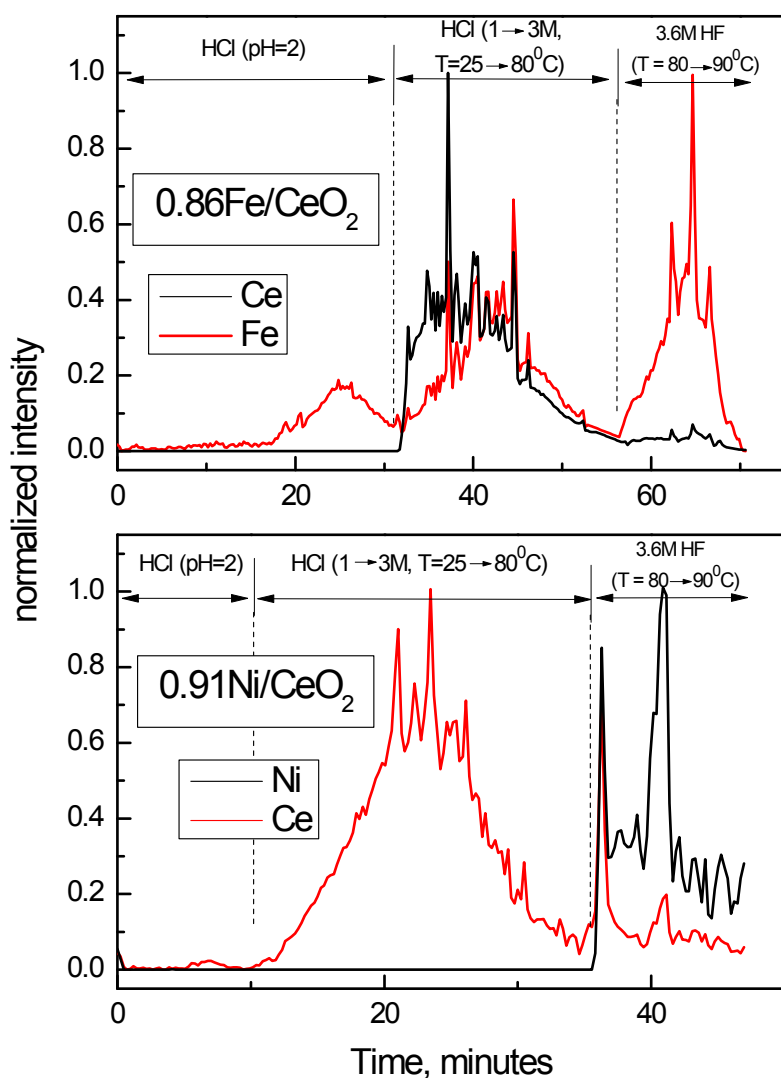


Fig.S1. Differential dissolution phase analysis spectra of 0.86Fe/CeO₂ and 0.91Ni/CeO₂ samples.

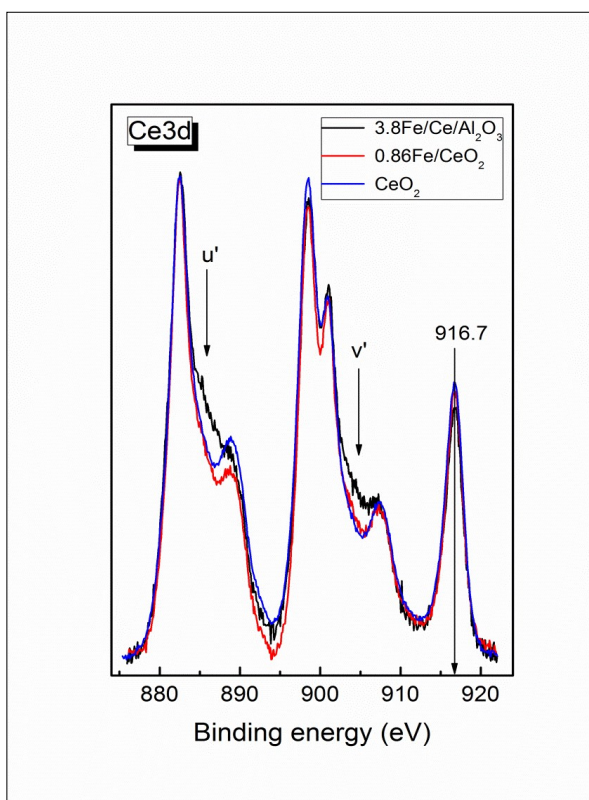


Fig. S2. Ce3d spectra of CeO₂, 0.86Fe/CeO₂ and 3.8Fe/Ce/Al₂O₃ samples.

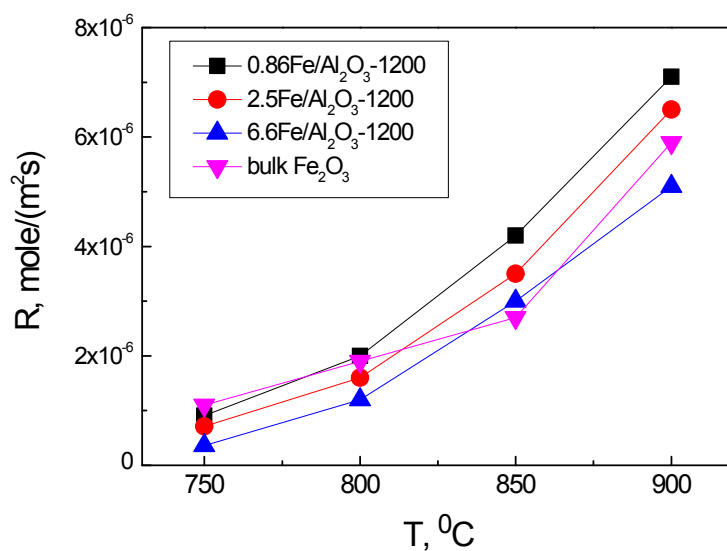


Fig.S3. Activity of different Fe/Al₂O₃-1200 and bulk Fe₂O₃ samples in the reaction of N₂O decomposition.

Temperature-programmed isotopic exchange (TPIE) O₂.

Oxygen isotopic exchange in a temperature-programmed mode (TPIE) was used to characterize oxygen mobility in the samples. Before every experiment, sample loaded

into a reactor (quartz tube, i.d. = 3 mm) was kept in 0.5% vol.¹⁶O₂+He flow at 900°C for 30 minutes, then the reactor was cooled down to room temperature in the same flow. At T≤100°C this mixture was replaced stepwise by the same one but containing ¹⁸O₂ and Ar (1 vol.%) as an inert tracer, and the reactor was heated up to 900°C (rate of heating 14.7^o/min). Gas flow rate and catalyst loading were the same in all experiments and amounted to 5.0 l/h and 0.025 g, respectively. Transient changes in the gas isotopic composition (¹⁶O₂, ¹⁶O¹⁸O and ¹⁸O₂ concentrations) were continuously monitored by mass spectrometry. ¹⁸O atomic fraction in the gas phase $\alpha_g(t)$ calculated as $\alpha_g(t) = ({}^{16}\text{O}^{18}\text{O} + 2{}^{18}\text{O}_2) / 2 \sum O^i O^j$, where $\sum O^i O^j = {}^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + {}^{18}\text{O}_2$ was a characteristic of the rate of oxygen exchange.

Change of $\alpha_g(t)$ during the TPIE on 0.86Fe/CeO₂ and 2.5Fe/CeO₂ samples have been shown in the Fig.S4. One can see that $\alpha_g(t)$ curve for 2.5Fe/CeO₂ sample is shifted towards higher temperatures thus meaning lower rate of exchange compared with that in 0.86Fe/CeO₂.

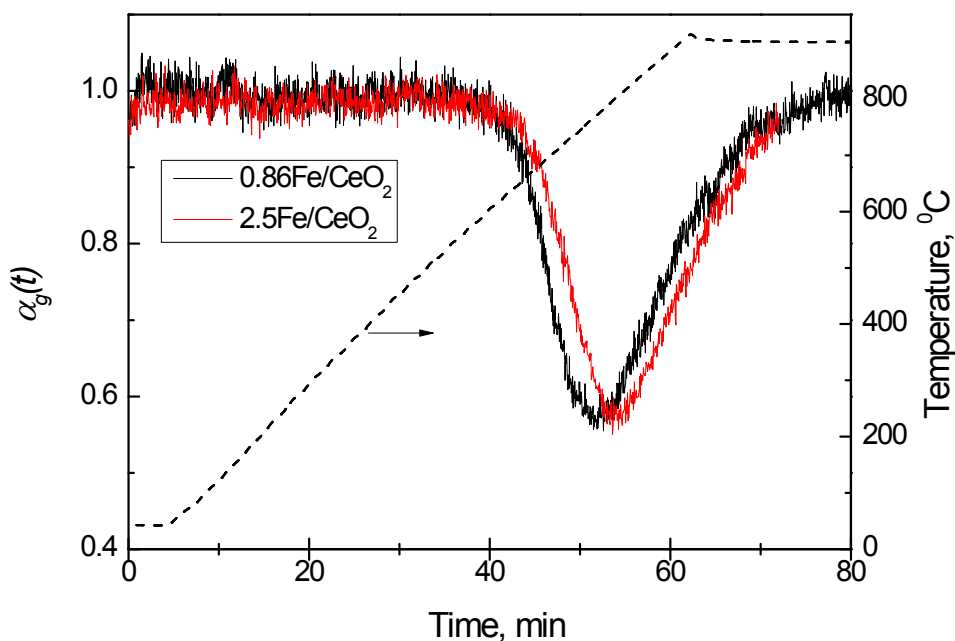


Fig.S4. $\alpha_g(t)$ variation with time for 0.86Fe/CeO₂ and 2.5Fe/CeO₂ samples during TPIE.

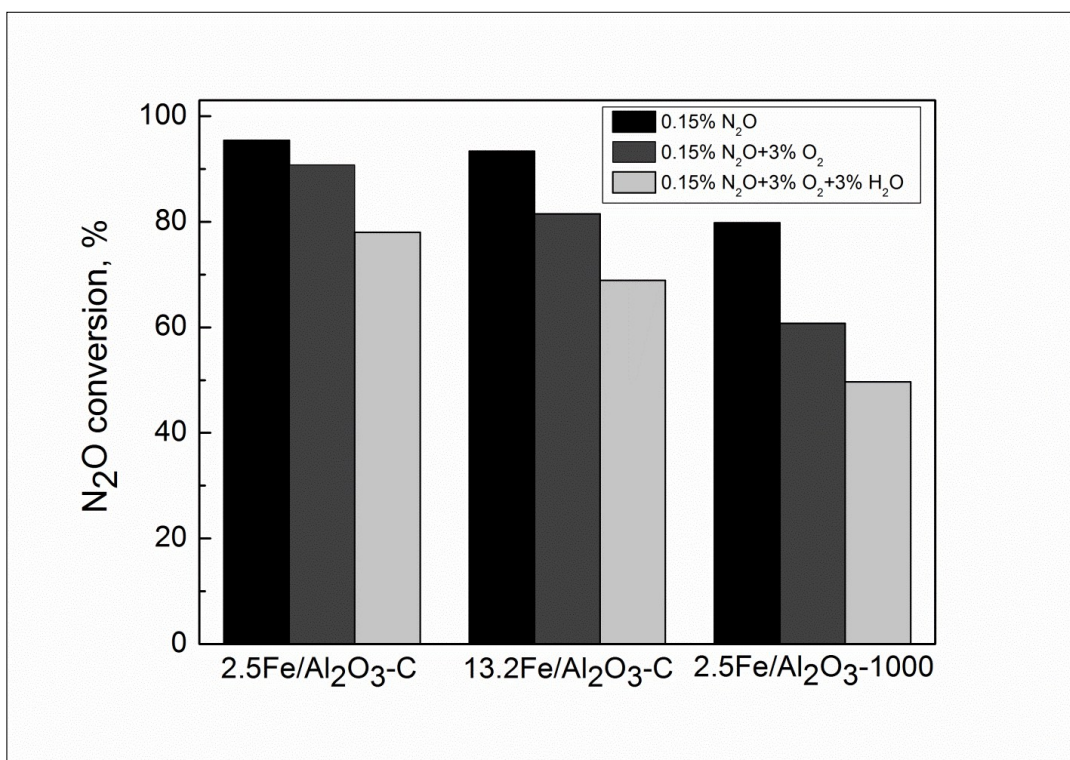


Fig. S5. Effect of O₂ (3 vol.%) and H₂O (3 vol.%) addition to 0.15%N₂O in He mixture on N₂O conversion at 900 °C.

O₂ TPD.

TPD O₂ experiments were carried out for the powder with 250 – 500 μm size fraction in a plug-flow quartz reactor coupled to QMS-200 mass-spectrometer. Before each experiment, the samples were heated in the flow containing 20%O₂ in He up to 900 °C, then conditioned for 30 min and cooled down to room temperature in the same flow. Finally, heating from room temperature to 900 °C at a rate 10 °C/min was performed in He flow. Flow rate was the same in all stages of TPD experiment and amounted to 18 cm³/min. A quantity of 200 mg was used for each test.

We didn't observe any O₂ desorption from CeO₂, NiO, Fe₂O₃ and supported 0.86Ni(Fe)/CeO₂ and 2.5Me/Al₂O₃ samples during temperature programmed desorption up to 900°C. In the samples 0.86%Co/CeO₂ and bulk Co₃O₄ obtained by calcination of Co(NO₃)₂ at 900°C evolution of O₂ into gas phase started at 750°C (Fig. S6). However, TPD peaks were characterized by different T_{max} values (820°C for supported and ≥903°C - for massive oxide). Desorption of about 1.3·10¹⁹ O₂ mol/g from 0.86%Co/CeO₂ containing 8.7·10¹⁹ Co at/g can correspond to reduction of Co₃O₄ to

CoO that is already reported both for bulk CoO and for Co-CeO₂ solid solutions [10, 11] without participation of oxygen from CeO₂ lattice. In this case lower value of T_{max} for 0.86%Co/CeO₂ can be explained by stronger diffusion limitation in bulk oxide characterized by S_{BET} value at 0.2 m²/g.

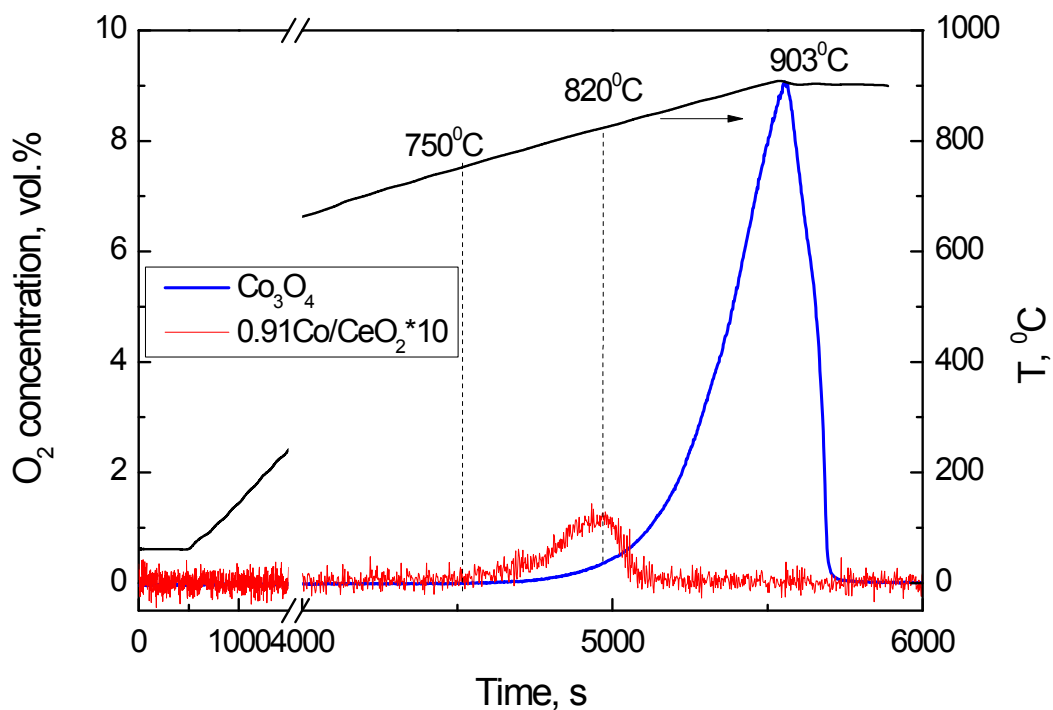


Fig. S6. O₂ desorption during TPD in He from bulk Co₃O₄ and 0.91Co/CeO₂ samples.

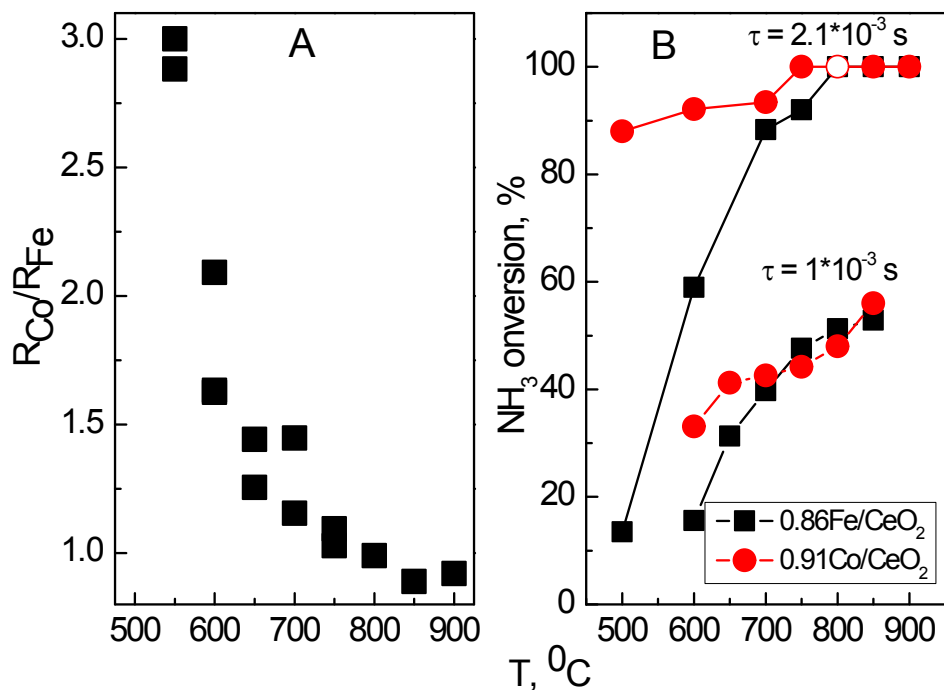


Fig.S7. Temperature dependency of: A – ratio of the rates of N_2O decomposition on $0.91Co/CeO_2$ (R_{Co}) and $0.86Fe/CeO_2$ (R_{Fe}) samples, B – NH_3 conversion at different contact times (τ).

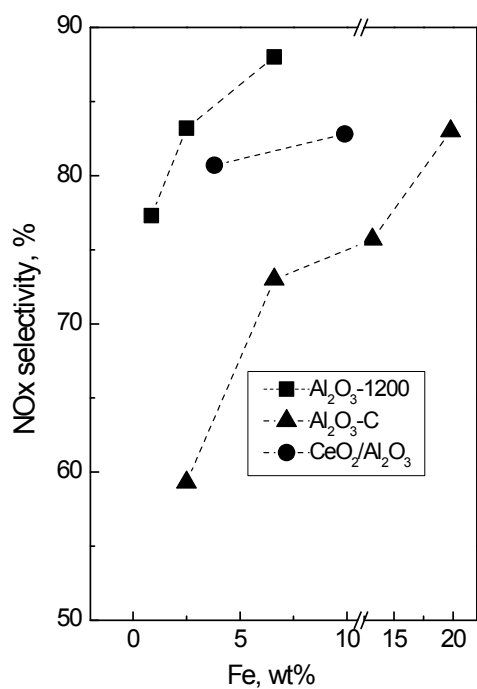


Fig. S8. NO_x selectivity depending on Fe content in Al_2O_3-1200 , Al_2O_3-C , and Ce/Al_2O_3 based samples at $800^{\circ}C$. Catalyst charge 0.015 g, gas flow rate 25 l/h.