

Formation of N_3^- during interaction of NO with reduced ceria

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

1. Background spectra of the oxidized and reduced ceria

The spectrum of the activated $\text{CeO}_2(\text{A})$ sample (Figure S1, spectrum a) contains bands in the OH region that are typical of ceria.¹⁻⁵ In particular, the most intense band at 3654 cm^{-1} and the shoulder at 3635 cm^{-1} are assigned to two kinds of type II hydroxyls, (i.e., oxygen bound to two cerium cations).¹⁻⁵ The weak band at 3494 cm^{-1} is attributed to type III hydroxyls.³ In agreement with published reports,^{1,2} after reduction the spectrum in the OH region changes, and the type II OH bands are shifted to 3680 and 3640 cm^{-1} .

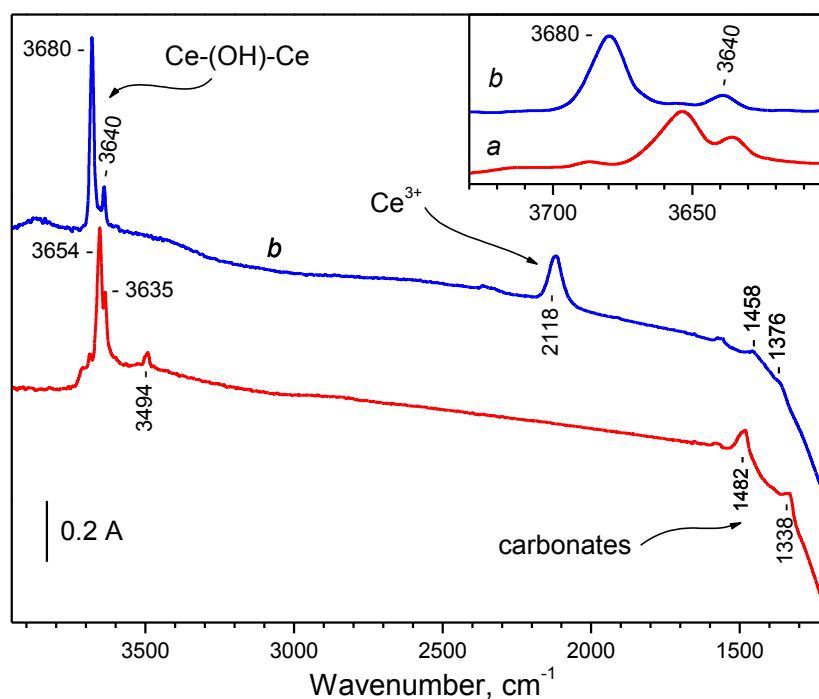


Figure S1. FTIR spectra of activated (a) and reduced (b) $\text{CeO}_2(\text{A})$ sample.

Two bands, at 1482 and 1338 cm^{-1} , are observed with the oxidized sample and are assigned to residual carbonate structures that are normally present on activated samples.⁵⁻⁷ Reduction leads to a shift of the maxima of the carbonate bands to 1458 and 1376 cm^{-1} and decrease in their intensities (Figure S1, spectrum b).

Finally, a band at 2118 cm^{-1} was detected only with the reduced sample. It is due to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ electronic transitions of the Ce^{3+} ions formed during reduction⁸.

2. Adsorption of small amounts of NO and ${}^{15}\text{NO}$ on ceria

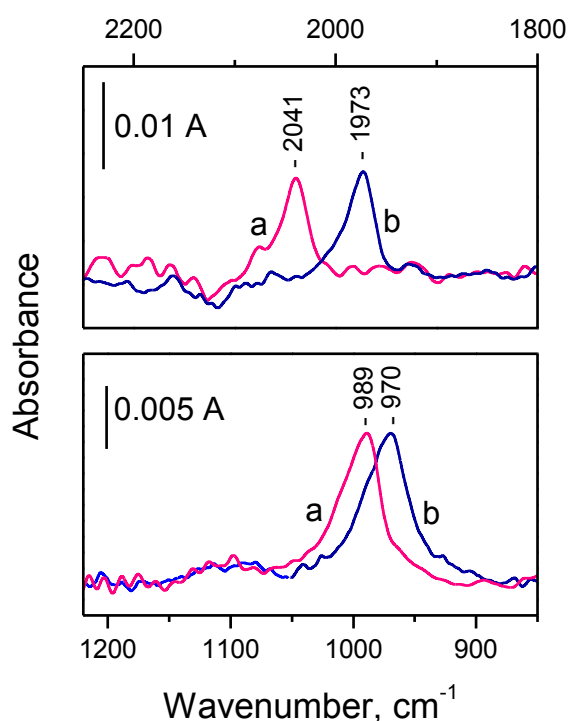


Figure S2. FTIR spectra of small amounts ($10 \mu\text{mol g}^{-1}$) of NO (a) and ${}^{15}\text{NO}$ (b) adsorbed on reduced $\text{CeO}_2(\text{A})$ sample. The spectra are background corrected.

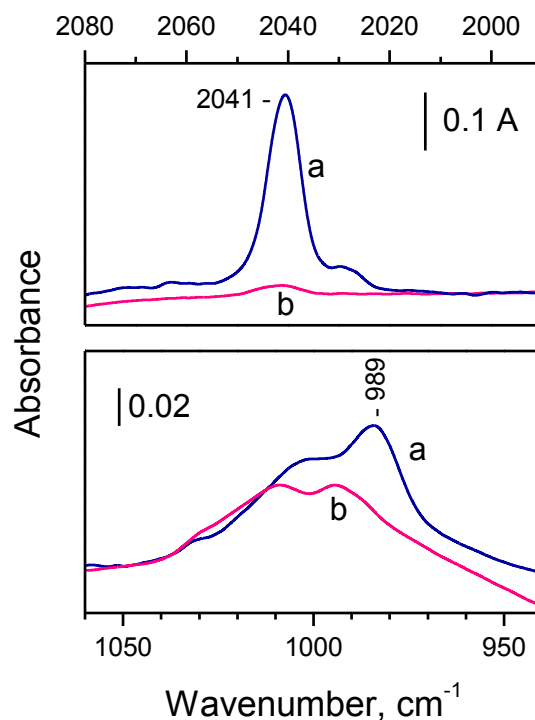


Figure S3. FTIR spectra of NO adsorbed on CeO₂(A) (a) and CeO₂(B) (b) samples. The spectra are chosen in order to show the maximal intensities in the bands in the region.

3. Statistical distribution of N₃⁻ species with different numbers of ¹⁵N atoms.

Consider the formation of N-N bond during NO adsorption. Adsorption of a 1 : 1 ¹⁴NO + ¹⁵NO isotopic mixture should lead to formation of species containing, in average, equal number of ¹⁴N and ¹⁵N atoms. Statistically, the following species should be formed in equal concentrations: ¹⁴N-¹⁴N; ¹⁴N-¹⁵N; ¹⁵N-¹⁴N and ¹⁵N-¹⁵N. If the two N-atoms are equivalent, the distribution will be: 25 % ¹⁴N-¹⁴N; 50 % ¹⁴N-¹⁵N; and 25 % ¹⁵N-¹⁵N.

In the case when an N-N-N bond is formed, according to the statistical distribution each of the following species will be with 12.5 % population: ¹⁴N-¹⁴N-¹⁴N, ¹⁴N-¹⁴N-¹⁵N, ¹⁴N-¹⁵N-¹⁴N, ¹⁵N-¹⁴N-¹⁴N, ¹⁴N-¹⁵N-¹⁵N, ¹⁵N-¹⁴N-¹⁵N, ¹⁵N-¹⁵N-¹⁴N and ¹⁵N-¹⁵N-¹⁵N. If the species are symmetric, the distribution will be: 12.5 % - ¹⁴N-¹⁴N-¹⁴N; 25 % - ¹⁴N-¹⁴N-¹⁵N, 12.5 % ¹⁴N-¹⁵N-¹⁴N; 12.5 % ¹⁵N-¹⁵N-¹⁵N; 25 % - ¹⁴N-¹⁵N-¹⁵N and 12.5 % ¹⁴N-¹⁵N-¹⁴N. Therefore, in this case 6 types of species will be observed and

the concentration of the species having one terminal N atom differing from the others will be two times higher than the concentration of the other species.

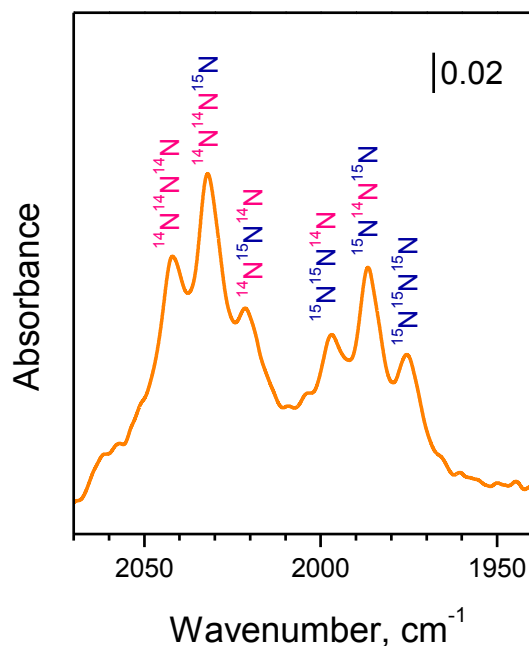


Figure S4. FTIR spectra of azide ions produced after adsorption of a $^{14}\text{NO} + ^{15}\text{NO}$ isotopic mixture (molar ratio ca. 3 : 2) on reduced ceria. The isotopic distribution of labelled.

This is consistent with the spectrum shown on Fig. S3. The slightly higher intensity of the bands characterizing ^{14}N -rich species is due to the slightly higher concentration of ^{14}NO in the $^{14}\text{NO} + ^{15}\text{NO}$ isotopic mixture.

4. Oxidation of azide species on ceria

They azide species on ceria are highly stable at 298 K in the presence of NO at low equilibrium pressure. At high NO equilibrium pressure the azide bands slowly start to decrease in intensity. Similarly, the azides are stable in presence of O_2 alone at 298 K. Figure S4 demonstrates the effect of successive addition of small dosed of O_2 to azide species formed after NO adsorption (present in the gas phase). The gradual disappearance of the azide bands in the co-presence of NO and O_2 is seen. Note that no intermediate bands in the region were observed. Note that, except of the slight shift of the azide bands, the only effect if a gradual decrease in intensity and ultimate disappearance. No intermediate bands assignable to N-N bonds were detected.

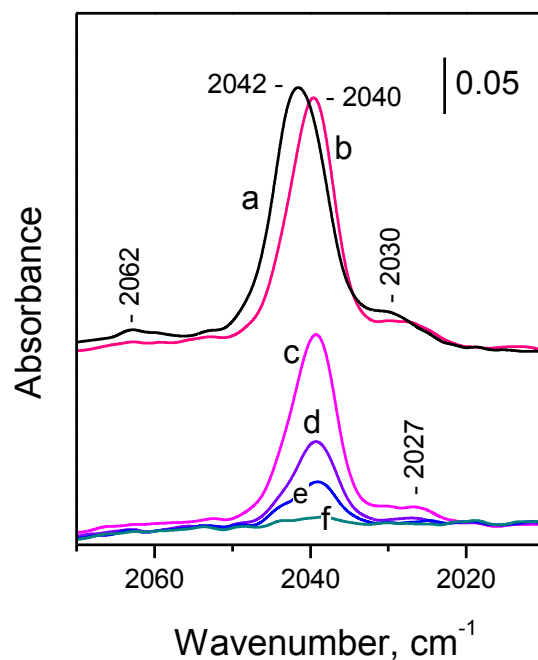


Figure S5. Azide species formed on reduced CeO₂(A) sample after adsorption of a NO at equilibrium pressure of 300 Pa) (a) and development of the spectra after successive addition of small amounts of O₂ to the system (b-f). The spectra are background corrected.

REFERENCES:

- 1 Badri, A.; Binet, C.; Lavalley, J. C., *J. Chem. Soc., Faraday Trans.* 1996, 92, 4669–4673.
- 2 Daturi, M.; Finocchio, E.; Binet, C.; Lavalley, J. C.; Fally, F.; Perrichon V., *J. Phys. Chem. B* 1999, 103, 4884–4891.
- 3 Agarwal, S.; Lefferts, L.; Mojet, B. L., *ChemCatChem* 2013, 5, 479–489.
- 4 Farra, R.; Wrabetz, S.; Schuster, M. E.; Stotz, E.; Hamilton, N. G.; Amrute, A. P.; Pérez-Ramírez, J.; López, N.; Teschner, D., *Phys. Chem. Chem. Phys.* 2013, 15, 3454–3465.
- 5 Vayssilov, G. N.; Mihaylov, M.; Petkov, P. St.; Hadjiivanov, K. I.; Neyman, K., *J. Phys. Chem. C* 2011, 115, 23435–23454.
- 6 Martínez-Arias, A.; Soria, J.; Conesa, J. C.; Seoane, X. L.; Arcoya, A.; Cataluña, R., *J. Chem. Soc., Faraday Trans.* 1995, 91, 1679–1687.
- 7 Niwa, M.; Furukawa, Y.; Murakami, Y., *J. Colloid Interface Sci.* 1982, 86, 260–265.
- 8 Binet, C.; Badri, A.; Lavalley, J.-C., *J. Phys. Chem.* 1994, 98, 6392–6398.