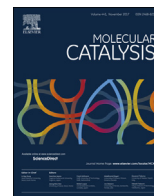




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journal homepage: www.elsevier.com/locate/mcatSpecies formed during NO adsorption and NO + O₂ co-adsorption on ceria: A combined FTIR and DFT studyMihail Y. Mihaylov^a, Elena Z. Ivanova^a, Hristiyan A. Aleksandrov^b, Petko St. Petkov^b, Georgi N. Vayssilov^b, Konstantin I. Hadjiivanov^{a,c,*}^a Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria^b Faculty of Chemistry and Pharmacy, University of Sofia, 1126 Sofia, Bulgaria^c Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

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ABSTRACT

Adsorption of NO and co-adsorption of NO and O₂ on ceria have been re-investigated by FTIR spectroscopy. To provide unambiguous assignments of the IR bands, adsorption of ¹⁵NO and co-adsorption of ¹⁴NO + ¹⁵NO isotopic mixtures have also been studied and DFT calculations performed. At the initial adsorption stages mainly symmetric nitrite species (2472, 1304, ca. 1160 and 822 cm⁻¹) and *trans*-hyponitrites ([N₂O₂]²⁻, ca. 1100 cm⁻¹) are simultaneously produced as a result of NO disproportionation. At further stages non-symmetric NO₂⁻ species (1393 and 1014 cm⁻¹), N₂O (2240, 1252 cm⁻¹) and small amount of nitrates are formed. Nitrates are the only surface products of the thermal decomposition of the nitrites and hyponitrites. In the presence of small amounts of oxygen, the hyponitrites are very easily oxidized. In contrast, all nitrites increase in concentration after addition of small amount of O₂ to the NO/CeO₂ system but are gradually oxidized in the presence of higher amount of oxygen giving rise to different surface nitrates.

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1. Introduction

The NO_x emission control is one of the most topical current problems in the environmental chemistry. Among the different methods used to reduce the NO_x emissions, the catalytic processes are very important because of their low cost and high efficiency. Without any doubt, the most attractive possibility for NO neutralization is its direct decomposition to N₂ and O₂. However, this process is still far from practical application because of its very slow rate (high activation energy) and inhibition effect of oxygen and water [1]. The major technologies that are nowadays applied are selective catalytic reduction (SCR) of NO_x by ammonia (for stationary sources) and three-way catalysts (for mobile sources) [2–4]. Other technologies, such as catalytic storage-reduction, have also been commercialized, but many research groups are actively working to improve them [5,6]. There are presently many efforts to develop other routes for NO_x control.

The development of new DeNO_x technologies as well as the improvement of the known ones require detailed knowledge on the nature of the surface species formed and distinguishing between

intermediates and spectator species. There are thousands of studies dealing with the nature of the surface nitrogen oxo-species formed after adsorption of nitrogen oxides or their co-adsorption with different reactants on various materials. The main products that have been reported to be formed after adsorption of NO can be divided into neutral species (nitrosyls, dinitrosyls, adsorbed N₂O, N₂O₃, NO₂ and N₂O₄), positively charged moieties (NO⁺, NO₂⁺) and anionic species (NO⁻, NO₂⁻, hyponitrites, nitro-nitrito and nitrate species) [1]. FTIR spectroscopy is the most used technique for spectral identification of these species [7].

The final desired product of NO_x conversion technologies is dinitrogen. This requires formation, at a certain stage, of N–N bonds. For NO decomposition neutral and charged NO dimers (e.g. hyponitrites) are often proposed as intermediates [8–13]. Selective catalytic reduction of NO_x with ammonia is believed to proceed via NH₄NO₂ or NH₄NO₃ intermediates [14,15]. When the reduction is performed with hydrocarbons, isocyanates are often proposed as key intermediates [16–19].

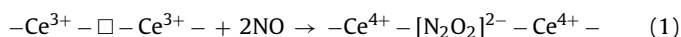
Ceria (CeO₂) is a key component in many catalysts for processes of considerable industrial and environmental interest [3,4,20–22]. These include catalysts for CO and soot oxidation [23–26], three-way catalysts [3,4], NO_x storage-reduction catalysts [5,6,27], low-temperature selective catalytic reduction of NO with NH₃ [28], etc. The main advantage of CeO₂ is related to its high oxygen release/storage capacity (OSC) due to the possibility of easy tran-

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sition between two oxidation states of Ce ion (4+ and 3+) and creating/filling oxygen vacancies in red-ox conditions [24,29]. To improve the catalytic performance of ceria many efforts were made by the researchers all over the world to elucidate the factors regulating the OSC, including synthesis method and pre-treatment conditions, shape, size and morphology of the CeO₂ nanoparticles, support, doping with foreign cations (with different size and oxidation state), metal-CeO₂ interaction, etc. [23–26,30,31]. Finally, to develop advanced catalyst systems identification of adsorbates and intermediates during the process is needed. In particular, there are many works dealing with the nature of the NO_x surface species formed on ceria [32–41] and ceria-based materials [37,38,41,42].

A pioneering IR study of NO adsorption on CeO₂ was reported by Niwa et al. [32]. These authors found bands at 1270 and 1160 cm⁻¹, assigned to the ν_{as} and ν_s modes, respectively, of chelating NO₂⁻ species and a band at 1090 cm⁻¹, attributed to *trans*-hyponitrite species. All these bands were proven to characterize vibrations involving N-atoms by parallel experiments on ¹⁵NO adsorption. In a subsequent study, Martinez-Arias et al. [33] proposed similar interpretation: they assigned bands at 1275, 1160 and 823 cm⁻¹ to chelating nitrites and a band at ca. 1100 cm⁻¹, to *trans*-hyponitrite species. The authors detected also bands at 1015 and 954 cm⁻¹ which were assigned, together with a suggested band at 1350 cm⁻¹, to *cis*-hyponitrites, as well as a band at 1174 cm⁻¹, supposed to characterize another type of nitrite species or NO⁻. In addition, bands assigned to nitrates (1505, 1305 and 1060 cm⁻¹) and adsorbed N₂O (2238 and 1255 cm⁻¹) were recorded. It was suggested that hyponitrites were formed by reaction of NO with two neighboring Ce³⁺ sites:



(where □ is an oxygen vacancy).

Upon heating, nitrites further react with surface oxygen, yielding nitrates, whereas hyponitrites decompose to N₂O.

Philipp et al. [35,36] examined interactions of CeO₂ with NO and NO/O₂ mixtures at different temperatures (323–573 K). They reported that NO adsorption led mainly to the appearance of nitrite species. Furthermore, according to these authors, *trans*-N₂O₂²⁻ (1097 cm⁻¹) and *cis*-N₂O₂²⁻ (1021 and 974 cm⁻¹) species were suggested to appear below 373 K; above 373 K only the *cis*-isomer was stable.

Azambre et al. [37,38] reported that adsorption of NO and NO₂ at room temperature on ceria and ceria-zirconia samples led mainly to the formation of bidentate nitrites and/or NO⁻ (1195–85 cm⁻¹) and *cis*-N₂O₂²⁻ (1360–20 and 1070–40 cm⁻¹). Simultaneously with (hypo)nitrite/NO⁻ formation, a consumption of bridged OH groups was observed and broad feature in the 3600–3000 cm⁻¹ range developed. Therefore, the main adsorption pathway was suggested to involve the reaction of NO with OH groups to produce adsorbed H₂O–HNO₂ complexes (3585–70, 1700–1620, 1550–1300 cm⁻¹) and their decomposition products, namely NO₂⁻, NO⁻, and/or HNO⁻ species. Nitrosyl anions can dimerize to yield hyponitrites, N₂O₂²⁻, easily decomposing to N₂O (2240 and 1255 cm⁻¹) and N₂.

Qi et al. [40] studied co-adsorption of NO and O₂ on manganese-ceria mixed oxide and detected bands, assigned as follows: 1530 cm⁻¹, nitrates; 1240 cm⁻¹, ν_{as} of nitrites; 1422 cm⁻¹, ν(N–N) of *trans*-hyponitrites; 1350, 1013 and 930 cm⁻¹, *cis*-hyponitrites; and 1180 cm⁻¹, NO⁻.

Recently, Zhang et al. [39] reported that NO adsorption on activated ceria results in formation of different kinds of nitrates (1608, 1575, 1535, 1485, 1305, 1276 and 1230 cm⁻¹) as well as to *trans*-hyponitrites (1442 cm⁻¹). On reduced samples they detected a complementary band at 1176 cm⁻¹ (assigned to NO⁻), bands at 1442 and 1385 (*trans*-hyponitrites) and bands at 1371 and 1358 cm⁻¹ (*cis*-hyponitrites).

This short survey shows that the assignment of the IR bands is rather controversial and not supported by additional experiments. In particular, we have impeached the proposed assignments to NO⁻ [43]. Indeed, the NO bond order in these species is ca. 2 and the reported frequencies in bulk species are around 1400 cm⁻¹, at definitely higher frequency than the bands proposed to characterize NO⁻ on ceria. Also, the assignments to different kinds of hyponitrite species are tentative. In fact, these species could be easily proven by co-adsorption of ¹⁴NO and ¹⁵NO isotopic mixtures. However, no such studies were performed and the only isotopic labelling applied just confirmed the participation of N atom in particular vibrations.

Taking into account the increasing number of studies on ceria-based materials for DeNO_x purposes, we believe that detailed and unambiguous determination of the nature of the nitrogen-oxo species formed on ceria is topical. Therefore, we have decided to reinvestigate the nature of the NO_x species formed on CeO₂. As a first step of this, we have studied interaction of NO with reduced ceria [43,44]. Using isotopically labelled NO we have concluded on the formation of N₃⁻ and NO²⁻ species (not reported before) at the initial stages of the interaction between NO and reduced ceria. In this study we report our results on the interaction of NO and NO + O₂ with non-reduced ceria and also provide data on the stability and reactivity of the surface species formed. To strengthen the assignments, parallel experiments were performed with ¹⁴NO and ¹⁵NO, and, in particular cases, with a mixture of the two adsorbates.

2. Experimental

2.1. Experimental details

Most experiments were performed with a CeO₂ sample supplied from Daiichi (purity 99.9%, specific surface area of 173 m² g⁻¹, average particle size of 46 nm). Some other samples were also investigated and the results were similar (see for instance Fig. S1 from the Supplementary Data).

The IR investigations were carried out using a Nicolet 6700 spectrometer (equipped with a MCT detector) at a spectral resolution of 2 cm⁻¹ and accumulating up to 128 scans. Self-supporting pellets (≈10 mg cm⁻²) were prepared by pressing sample powders at 100 kPa and were directly treated in the IR glass cell. The latter was connected to a vacuum apparatus with a residual pressure of about 10⁻⁴ Pa. Prior to the adsorption measurements, the samples were activated by calcination at 755 K for 1 h and evacuation for 1 h at the same temperature. Nitrogen monoxide (>99.0% purity) and O₂ (99.999) were purchased from Messer. ¹⁵NO was supplied by Isotec Inc. and was diluted in He (molar ratio of NO: He = 1: 10). Oxygen was additionally purified by passing through a liquid nitrogen trap. In some experiments (requiring low equilibrium pressure) NO was also passed through a liquid nitrogen trap.

2.2. Computational details

The calculations are performed using a periodic plane-wave DFT method with PW91 exchange-correlation functional of a generalized-gradient (GGA) type as implemented in the VASP program [45–48]. The stoichiometric and reduced ceria is described within the so-called GGA + U approach, in which on-site Coulombic interaction with U = 4.0 eV [49–51] is included. The kinetic energy cut-off is 415 eV. The calculations are performed as spin-polarized, where appropriate. Ceria is modelled as a nanoparticle Ce₂₁O₄₂OH (containing an extra OH group for charge balance after NO adsorption) with a diameter of 1.0 nm and it exhibits the crystallinity of the fluorite structure of CeO₂ that was previously used for the modelling of nanostructured ceria systems [52–54]. The space between neighboring slab images is 1.0 nm, which ensures that the lateral

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