The remarkable reaction of N_2O with a binary component lanthanide oxide mixture

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The interaction of N_2O with a Sm_2O_3–PrO_{2-x} mixed oxide proceeds *via* the unexpected production of a new bulk phase that has been tenatively assigned to a new *cis*-hyponitrite compound.

N_2O is present in minor quantities (from natural and anthropogenic sources[1]) in the atmosphere but remains an important greenhouse gas because of having a much greater global warming potential and a longer residence time than CO_2.[2,3] Precious metals,[4,5] zeolites,[6,7] perovskites[8] and lanthanide oxides[9] (and structurally related oxides[10–12]) have been suggested as catalysts for the reduction of N_2O at an oxide surface. It is generally thought that oxygen vacancies are necessary for reaction of the lanthanide oxides with N_2O by donation of electrons and then acceptance of the oxygen radical into the vacant site.[13] The lack of reactivity of stoichiometric oxide surfaces (there are exceptions where stoichiometric surfaces appear to react[14]) to N_2O allows this gas to be used as a titrant of metal surface sites in oxide supported catalysts.[15] In early work, Cerruti *et al.* found evidence for the formation of complex nitrogen oxide species at oxide surfaces[16] and it now seems that the reaction chemistry of N_2O at oxide systems is considerably richer and varied than these simplistic models indicate[10,12] and authors such as Gao and Au[12] and Bulushev *et al*[7] have reported limited activity of non-defective lanthanide and related oxide surfaces to N_2O. This paper details recent experiments showing that N_2O has previously unexpected reactivity with Sm_2O_3–PrO_2 and reports similar observations for other mixed lanthanide oxide surfaces.

Samples were prepared by basic co-precipitation from nitrate solutions (at the desired metal mol%) using tetramethylammonium hydroxide. Precipitates were vacuum filtered, washed several times, dried in air at 400 K and calcined in air at 823 K for 8 hours. These were ground and sieved to produce particles of 100 ± 20 μm in diameter. The mixture of 15% (metal mol%) Pr_2O_{2-x} in Sm_2O_3 is described as SmPr15. X-ray fluorescence spectroscopy (Panalytical Minipal) showed that the compositions were within 0.5% of target. Powder X-ray diffraction (XRD) data were collected on a Philips PW 3710 MPD instrument using Cu Kα radiation and standard θ–2θ reflection geometry. Diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) spectra were collected on a BIORAD FTIR apparatus. BET nitrogen adsorption data were collected using a Micromeritics Gemini 2375 machine after degassing samples for 16 h at 473 K. For reaction studies (all data reported are for room temperature adsorption) the samples were placed in a quartz tube through which gas could be flowed and held in place by a quartz frit and quartz wool. A quadrupole mass spectrometer was used for inlet/exit gas analysis by monitoring mass/charge fragments: 14, 16, 28, 32, 30, 44 and 46. 65 mg of samples were *in situ* cleaned in oxygen (20 ml min^{-1} at 573 K for a minimum of 8 h) and then cooled in the same gas (to ensure stoichiometry) prior to N_2O (20 ml min^{-1}, 3% N_2 in He) reaction. Uptake of gas was measured using temperature programmed desorption (heating rate of 20 K min^{-1}) in flowing He. The desorption flux was quantified by comparison to calibrated 5% mixtures in He (BOC).

XRD measurements (Fig. 1) were made following calcination at 823, 973 and 1273 K (8 h) and show that SmPr15 exhibits a crystallite structure readily assigned to the lanthanide oxide C-phase (cubic bixybite, (JCPDs file number 43-1029)). Peak width narrowing was observed as the calcination temperature was increased due to crystallite growth. There is no change in reflection 2θ position or appearance of new features with calcination and the data suggest that there is solid solution of the two oxides through this temperature rage. The BET derived surface area of the sample is 47.3 $m^2\ g^{-1}$ following 823 K calcination.

SmPr15 (calcined at 823 K) showed unexpectedly strong chemisorption of N_2O following exposure at room temperature. Indicative TPD data are shown in Fig. 2 as a function of exposure time. Only N_2O was observed in these TPD experiments and no evidence for N_2, NO, O_2 or other species was obtained. The TPD data apparently show a doublet feature but we believe this is a result of a very strongly endothermic process which is not adequately compensated for by the heating programme. Smaller samples in steel tubes gave singlet peaks but the data were too noisy for quantification. As can be seen from the TPD traces in

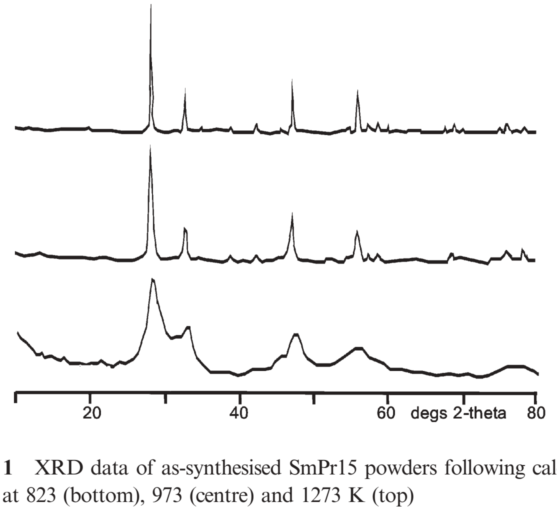

Fig. 1 XRD data of as-synthesised SmPr15 powders following calcination at 823 (bottom), 973 (centre) and 1273 K (top)

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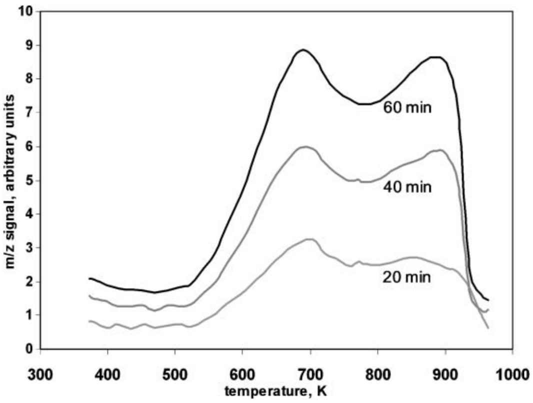

Fig. 2 N_2O-TPD data (m/z = 44) as a function of exposure time in minutes (as indicated in figure)

Fig. 2, there is an increase in adsorbed amount with time and periods of around 55 to 65 minutes yielded the maximum coverage. Longer exposure periods yielded lower uptakes which we believe is due to collapse of surface area related to a bulk reaction taking place. For the sample exposed for 1 hour the desorbed amount can be quantified as 3.02×10^{20} molecules. This can be equated to an uptake of 10.7 monolayers of N_2O using the surface area (47.3 $m^2\ g^{-1}$), an approximate surface site density of 1×10^{-19} atoms m^{-2} and assuming one N_2O molecule per surface site. This is clearly a reactive absorption process with the formation of a new compound rather than a simple surface adsorption. If the desorbed flux is compared to the number of moles of oxide used (assuming all metal atoms present as M_2O_3) the molar ratio of N_2O/M_2O_3 can be calculated as 2.93. Similar values were obtained using the breakthrough time (*i.e.* the time for N_2O to appear on switching the gas into the flow). The measured stoichiometry is consistent with the following reaction (eqn (1)):

$$3N_2O(g) + M_2O_3(s) \rightarrow M_2(N_2O_2)_3(s) \qquad (1)$$

DRIFTS data were used to identify the species produced by absorption of N_2O at these materials (Fig. 3). Strong IR absorption peaks were observed at 863, 1035 and 1348 cm^{-1}. These peak positions are similar to those observed for bulk *cis*-hyponitrite ($N_2O_2^{2-}$) in $Na_2N_2O_2$ namely 837 ($\nu_{s,N-O}$) cm^{-1}, 1047 ($\nu_{a,N-O}$) cm^{-1} and 1314 ($\nu_{N=N}$) cm^{-1}.[17] Similar peak positions for *cis*-hyponitrite species were observed for $K_2N_2O_2$.[18] Minority *cis*-hyponitrite $N_2O_2^{2-}$ species have been observed at some metal oxide surfaces including CeO_2 (954, 1015 and 1350 cm^{-1})[19] and La_2O_3 (822 and 1138 cm^{-1}).[20] The close agreement of the previous studies to the data provided here does suggest the formation of a bulk *cis*-hyponitrite species which is consistent with the stoichiometery suggested in eqn (1).

It has been long thought that reaction of N_2O with lanthanide oxide surfaces is *via* electron-containing oxygen vacancies.[9,11–13] However, all the proposed reaction schemes suggest that N_2O is dissociatively adsorbed and products such as N_2, NO, NO_2 and nitrates species are formed. Therefore, it is difficult to apply these schemes to the behavior observed here. Instead, we suggest that the formation of bulk *cis*-hyponitrite material is the result of a simple acid–base reaction. Klingenberg and Vannice have reported the formation of $N_2O_2^{2-}$ and NO^- at lanthana on NO exposure due to reaction with the strong Lewis base surface.[21] It is clear from the present work that the reaction of N_2O with lanthanide oxide surfaces is unusual and is a previously unobserved reaction pattern for N_2O and an oxide phase. The data challenge the accepted mechanisms for the interaction of nitrous oxide with oxide materials. The work also provides impetus towards a requirement for more extensive investigation of the N_2O interaction with oxide materials. Investigations we have carried out suggest this *cis*-hyponitrite formation may be a pattern of activity for the lanthanide oxides particularly mixtures of 3+ and 4+ valent materials.

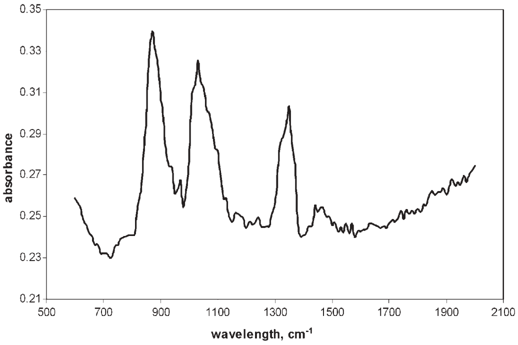

Fig. 3 DRIFTS spectrum recorded from SmPr15 sample following 1 hour exposure to N_2O.

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