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Oxygen-18 isotope exchange and equilibration processes over preoxidised and promoted ceria. Part I. $^{15}N^{18}O_{(g)}$ or $(^{18}O_2 + {}^{16}O_{2(g)})$

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Abstract

Changes effected in the isotopic composition of monolayer equivalent amounts of $^{15}N^{18}O$ or equimolar $(^{18}O_2 + {}^{16}O_2)$ probe gases by contact with pure or rhodia-promoted CeO_2 and ZrO_2 are reported and analysed. A prerequisite for efficient and selective promotion of the R_0-type homophase exchange process, $^{18}O_{2(g)} + {}^{16}O_{2(g)} \rightarrow 2\,{}^{18}O^{16}O_{(g)}$ at 295 K over preoxidised samples was dispersal thereon of ≥ 2 wt% rhodia originated from chloride-free precursors. Temperatures for onset of heterophase isotope exchange over preoxidised CeO_2 or ZrO_2 under T-ramp were 790 or 873 K. However, dispersion of 0.5, 2.0 or 4.0 at.% rhodia thereon resulted in onset of $^{18}O_{2(g)} + 2\,{}^{16}O^{2-}_{(s)} \rightarrow {}^{16}O_{2(g)} + 2\,{}^{18}O^{2-}_{(s)}$ heterophase exchange at progressively lower temperatures. Nature of the sites/mechanisms via which dispersed rhodia promotes those R_0 or R_2 changes in the dioxygen probe gases are considered. Also presented are results from analagous experiments in which $^{15}N^{18}O$ replaced dioxygen as probe gas over preoxidised CeO_2 or $RhO_x//CeO_2$. Observations under T-ramp demonstrated the onset at ca. 450 K of a decrease in $^{15}N^{18}O$ mirrored by onset of an increase in $^{15}N^{16}O$. Continuation of both processes at similar rates brought about an equimolar $(^{15}N^{16}O + {}^{15}N^{18}O)$ mixture at 700 K. The 1:1 stoichiometry of that conversion would be consistent with either of the R_1-type heterophase oxygen isotope exchange processes $^{15}N^{18}O_{(ads)} + {}^{16}O^{2-}_{(s)} \rightarrow {}^{15}N^{16}O_{(ads)} + {}^{18}O^{2-}_{(s)}$; or $^{15}N^{18}O_{(ads)} + {}^{16}OH^{-}_{(s)} \rightarrow {}^{15}N^{16}O_{(ads)} + {}^{18}OH^{-}_{(s)}$ over preoxidised CeO_2 or 0.5% $RhO_x//CeO_2$. Modifications of their activity and selectivity in $^{15}N^{18}O$ conversions following reductions in H_2 at 423 or 823 K are described and interpreted. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Isotope exchange; Homophase equilibrium process; Heterophase exchange process; Rhodia; Ceria

1. Introduction

Much valuable information on surface oxygen exchange and oxygen self-diffusion processes *at high temperatures* in ceria-containing solid oxide electrolytes [1,2] has emerged from recent R & D concerned with the development of solid oxide fuel cells, or with optimising the oxygen storage role of ceria in three-way-catalytic converters (TWCs) at the high temperatures they reach in continuous operation [3,4]. Much less abundant, however, is detailed updated information on oxygen exchange at *gas/ceria* interfaces, or at those between ceria and other metal oxides, at *moderate* temperatures – such as that experienced by TWCs during their brief periods of "warm-up from cold start". Unlike intensive study of roles of *group VIII metal//metal-oxide support* interactions during such periods [5] relatively little work has been published concerning interactions during early stages of

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warm-up when "preoxidised" better represents the surface condition of the group VIII component. Consequently "*group VIII metal oxide//oxidised ceria*" may be a truer representation of the microinterface condition which moderates transfer of oxygen to, or between, gaseous reactants such as nitric oxide or O_2, in early stage of warm-up. Efforts to mimic aspects of such microinterfaces and their activity in warm-up conditions have been made in this study (a) by preparing binary metal oxide powdered materials featuring rhodia dispersed on ceria and (b) observing their activities for *reaction/oxygen isotope exchange* with $^{15}N^{18}O$ and $(^{18}O_2 + ^{16}O_2)$ at temperatures in the "warm-up" range. Predominance of oxygen exchange or reaction processes occurring at, or within short distances from such interfaces [6], rather than the predominance of bulk diffusion of oxygen species often reported at higher temperatures [7–9] was sought by this approach.

In view of literature reports that ^{18}O labelled nitric oxide can exchange that label with the surface lattice $^{16}O^{2-}$ anions of some metal oxides at ambient temperature [10]; $^{15}N^{18}O$ was one of the probes here selected to test for such activity in CeO_2 or ZrO_2 powders when pure and when promoted by RhO_x dispersed thereon. An entropically non-equilibrated equimolar mixture of $(^{18}O_2 + ^{16}O_2)$ was also utilised as a probe gas in such tests, prompted by literature reports that some metal oxides can promote the homophase R_0-type oxygen isotope equilibration process $^{18}O_{2(g)} + ^{16}O_{2(g)} \Leftrightarrow 2^{18}O^{16}O_{(g)}$, at temperatures as low as 200 K [11,12]. In addition to testing the preoxidised ceria-containing solids for low temperature activity in changing the isotopic composition of $^{15}N^{18}O$ or $(^{18}O_2 + ^{16}O_2)$ during recirculation at room temperature, tests have been extended to include observations under T-ramp. Identifications are thus made *both* of onset-temperatures *and* of the nature of any heterophase oxygen isotope exchange process(es) between surface lattice $^{16}O^{2-}_{(s)}$ anions of the metal oxide and ^{18}O content of the labelled gas probes which eventually develop under adequate thermal activation [13,14]. A bias in sensitivity of present experimental procedures towards events involving single or pairs of surface $^{16}O^{2-}_{(s)}$, and away from those reported to require diffusion of $^{16}O^{2-}_{(b)}$ from bulk regions of the metal oxide was sought here as follows:

1. Arranging that the number of molecules of isotopically enriched probe gas introduced into contact with the metal oxide sample in a recirculatory reactor be similar to the total number of surface sites upon the metal oxide sample tested;
2. after equilibration at room temperature for 1–2 h, temperature of the reactor segment was ramped upward at 10 or 2°C min^{-1} with mass spectrum of the recirculating gas being recorded every 30 s;
3. ensuring adequate sensitivity in the mass spectrometric monitoring of isotopic composition of the gas-phase to detect appearance of isotopically exchanged species such as $^{15}N^{16}O$ or $^{18}O^{16}O$ at levels as low as 3% of the originally introduced probe gas, whilst retaining capability to follow decreases in the latter. Ideally such procedures should yield comparative values for onset temperatures at which thermal activation becomes sufficient for the most loosely bound $^{16}O^{2-}_{(s)}$ or $(^{16}O^{2-}_{(s)} \ldots ^{16}O^{2-}_{(s)})$ pair species to become involved in exchange.

2. Experimental

2.1. Materials

The isotopically labelled probe gases, viz. $^{15}N^{18}O$ enriched to 99% in both ^{15}N and ^{18}O, and also the equimolar $(^{18}O_2 + ^{16}O_2)$ mixture were used "as supplied" by Isotech. Ceria powder available commercially from Rhone Poulenc (CeO_2(r.p.), BET$\sim$110 $m^2 g^{-1}$) was utilised as high surface area support. An "ex-nitrate" ceria support, free from La^{3+} impurities, was prepared 'in-house' by precipitation from solution of high purity $Ce(NO_3)_3$. ZrO_2 and Rh_2O_3 powders were obtained from Degussa and Johnson Matthey, respectively. All were precalcined at 823 K in a flow of pure O_2 for 2 h, to decrease surface concentrations of the hydroxides or carbonaceous impurities before use as supports for rhodia. Deposition of rhodia thereon, en-route to RhO_x// CeO_2 or to RhO_x/ZrO_2 was usually achieved via "incipient wetness" with an appropriate small volume of a non-aqueous solution of rhodium acetyl-acetonate (termed "ex-Rh(acac)$_3$"), followed by drying and a second 2 h calcination in O_2 at 823 K. An estimate of the number of $^{16}O^{2-}_{(s)}$ anions in the outermost surface layer of 300 mg of CeO_2 having BET of 110 $m^2\,g^{-1}$ was 16×10^{19}. The number of gas-probe molecules of $^{18}O_2$ introduced into the recirculatory reactor and recirculated over the CeO_2 was 7×10^{19}. On the basis of a dispersion of 66% measured for 0.5% RhO_x upon ceria, the number of $^{16}O^{2-}_{(s)}$ related to rhodia were 5.8×10^{18}. Incipient wetness by an aqueous solution of $RhCl_3$ was occasionally used en-route to "ex-chloride" RhO_x//CeO_2 or RhO_x/ZrO_2 for comparison with the ex-Rh(acac)$_3$ materials. Co-precipitated RhO_x–CeO_2 and $Ce_xPr_{1-x}O_2$ materials were prepared from aqueous solutions containing $Ce(NO_3)_3$ and $Rh(NO_3)_3$ or $Pr(NO_3)_3$ in desired mole proportions, from which precursors of the mixed oxides were precipitated, followed by filtration, repeated washings, drying and calcination for 6 h in O_2 at 823 K.

2.2. *Characterisations*

Temperature programmed reduction profiles in H_2 (TPR-H_2) were performed in the conventional manner upon all materials and yielded excellent agreement with the published work [15]. Well-known problems, arising from spillover of hydrogen species onto ceria from metallic rhodium [16] make it very difficult to obtain reliable values for dispersion of metallic rhodium upon ceria by conventional H_2-uptake methods [17]. A modification of that method, developed by Trovarelli et al. [18] to circumvent the hydrogen-spillover problem, was used to arrive at estimates for the dispersion of RhO_x upon ceria and other supports. In one respect the method is indirect, since it requires that the dispersed RhO_x species be first converted to dispersed metallic rhodium particles by mild prereduction in H_2 and assumes that the dispersion then measured for $(Rh^0)_n$ by CO adsorption thereon is closely similar to that which applied to $(RhO_x)_n$ prior to the mild prereduction.

2.3. *Measurements of oxygen isotope exchange*

These were made by bringing a low pressure (3–5 mbar) of $^{15}N^{18}O$ or $^{18}O_2+^{16}O_2$ into contact with an in situ preoxidised sample (300 mg) of the chosen metal oxide, within an all-glass recirculatory system equipped for repetitive mass spectrometric (MS) analysis of the recirculating gas. The following sequence of MS measurements thereon were made upon each gas/metal-oxide system in closely similar conditions, with a view to enhancing inter-material comparability between results detailing the profiles for: (i) time-dependent changes in isotopic composition of the initially introduced $^{15}N^{18}O$ or $(^{16}O_2+^{18}O_2)$ probe gas at r.t. (if any); (ii) subsequent thermally induced changes upon application of a temperature ramp at 10 or 2°C min^{-1}. Extent of realization of our objective of only comparing changes smaller in magnitude than values of the number of $^{16}O^{2-}_{(s)}$ species in the surface monolayer of the CeO_2 or RhO_x//CeO_2 materials (see values above) can be adjudged from values given in the Section 3.

It proved possible, for all measurements using $(^{18}O_2+^{16}O_2)$, to maintain an in-loop trap at 77 K, thereby ensuring negligible partial pressures of H_2O or CO_2 in the recirculating gas, and so averting any possibility for contribution by such trace impurities to changes in the isotopic composition of dioxygen in those conditions. However, tests with 5 mbar $^{15}N^{18}O$ as the sole recirculating probe gas, whilst maintaining various refrigerants on the trap, yielded erratic behaviour of unknown origin. Consequently, profiles based on $^{15}N^{18}O$ as the probe gas were made without refrigerant on the trap, with the result that elimination of possible influences of traces of water or surface hydroxyls [19,20] was not assured.

3. Results and discussion

3.1. *Using $^{15}N^{18}O$ as isotopically labelled probe molecule*

$^{15}N^{18}O_{(g)}$//$CeO_{2(s)}$: The stepwise procedure utilised for introduction of the 5 mbar $^{15}N^{18}O$ into contact with in situ preoxidised CeO_2 did not allow evaluation of the extent of initial adsorption at r.t. The only alterations in gas phase composition detected by mass spectrometry during recirculation over preoxidised, high surface area CeO_2 for 0.5 h at room temperature were limited increases of 1.2×10^{19} molecules each of $^{15}N^{16}O$ and of $^{15}N_2$. Those changes implied: (i) dissociation of a fraction of $^{15}N^{18}O$ reactant upon a limited number of oxygen-accepting surface sites, thereby producing adsorbed ^{15}N-atom fragments; and their pairwise combination to yield $^{15}N_2$ at the

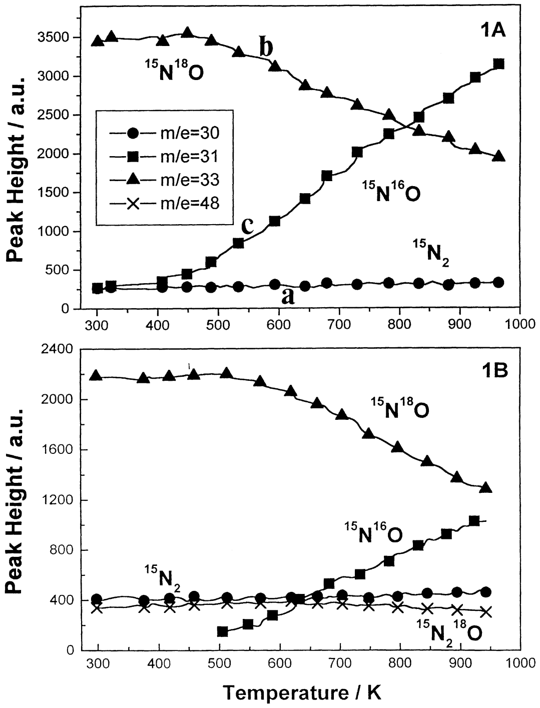

Fig. 1. (A) Composition of the gas phase arising from r.t. contact of 5 mbar $^{15}N^{18}O$ with preoxidised ex-nitrate CeO_2 (cf. points on l.h.s. of (A)); and profiles for subsequent changes under T-ramp at the rate of 10°C min^{-1}. (B) Data at equivalent stages after contact with H_2-pre-reduced CeO_2 (HTR-823 K).

low level indicated on the l.h.s. axis of Fig. 1(A); (ii) on the basis of equally low yield of $^{15}N^{16}O$, that reaction of ^{15}N fragments with the abundant capping $^{16}O^{2-}_{(s)}$ anions upon the oxidised ceria surface were very ineffective at r.t. Plots a–c of Fig. 1(A) illustrate profiles of changes in gas phase composition, observed whenever a T-ramp at 10°C min^{-1} was applied to the reactor segment of the recirculatory system: (a) demonstrates that extent of $^{15}N_2$ was not significantly increased from the limited value achieved at r.t., implying that no significant increase in number of $^{15}N^{18}O$-dissociating sites resulted during heating to ca. 900 K; *(b)* shows a contrasting marked decrease in $^{15}N^{18}O$ onsetting at 473 K with an average slope equivalent to 2.7×10^{19} molecules converted over its first 200 K; *(c)* illustrates the appearance and progressive increase in $^{15}N^{16}O$, rising rapidly above 473 K with an average slope equivalent to 4.3×10^{19} molecules produced over 200 K. Since the latter was significantly larger than in plot (b) over the same range, this implied an additional contribution to $^{15}N^{16}O$ formation by $^{15}N^{18}O_{(ads)}$ stored on the ceria from initial adsorption. The principal features of plots (b) and (c) in Fig. 1(A) thus indicate that the dominant thermally induced process at the $^{15}N^{18}O$//oxidised CeO_2 interface at T-ramp $\geq$473 K was oxygen isotope exchange as per Eq. (1a) and Eq. (1b), and that such exchange approached at 900 K the equivalent of the estimated number of $^{16}O^{2-}_{(s)}$ capping oxygens on the ceria sample. Preoxidised ceria thus joins a select group of metal oxides capable of facile exchange of their surface oxygen ions with the oxygen of nitric oxide [10]. Representation of the stoichiometry of the process as per Eq. (1a) and Eq. (1b) – showing only *single*$-^{18}$O for *single*$-^{16}$O exchange events are conventionally termed R_1-type. (Identical effect upon isotopic composition of the nitric oxide could possibly result from interaction with $^{16}OH^{-}_{(s)}$ surface hydroxyls rather than $^{16}O^{2-}_{(s)}$.).

$$R_1\text{type}:\quad {}^{15}N^{18}O_{(g)} + {}^{16}O^{2-}_{(s)} \rightarrow {}^{15}N^{16}O_{(g)} + {}^{18}O^{2-}_{(s)} \tag{1a}$$

$$R_1\text{type}:\quad {}^{15}N^{18}O_{(ads)} + {}^{16}O^{2-}_{(s)} \rightarrow {}^{15}N^{16}O_{(g)} + {}^{18}O^{2-}_{(s)} \tag{1b}$$

On the basis of strong similarities between H_2-TPR profiles measured here for the preoxidised ceria used in the present study (cf. Fig. 2(A)), and those reported and interpreted in the literature [15], removal of a substantial fraction of surface $^{16}O^{2-}$ from ceria was to be expected from an in situ pretreatment with H_2 at 823 K [HTR-823 K] but only a very much lower fraction after [LTR-423 K]. This led us to compare two sets of profiles for $^{15}N^{18}O$ conversions over differently pretreated CeO_2 samples: one originated from contact of LTR-423 K ceria with 5 mbar $^{15}N^{18}O$, and the other from contact of HTR-823 K ceria. Profiles for $-\Delta^{15}N^{18}O$, $+\Delta^{15}N^{16}O$ and $+\Delta^{15}N_2$ from the LTR-423 K ceria were qualitatively very similar to those in Fig. 1(A) for the preoxidised ceria. This reinforced our view that profiles of $^{15}N^{18}O$ and $^{15}N^{16}O$ versus ramp temperature mainly originated from thermally induced exchange with surface $^{16}O^{2-}_{(s)}$ or $+^{16}OH^{-}_{(s)}$ of ceria, and not from an artefact involving interchanges between $^{18}O_{2(g)}$ and adsorbed $^{16}O_2$ possibly retained from the in situ preoxidation process. The following significant differences were, how-

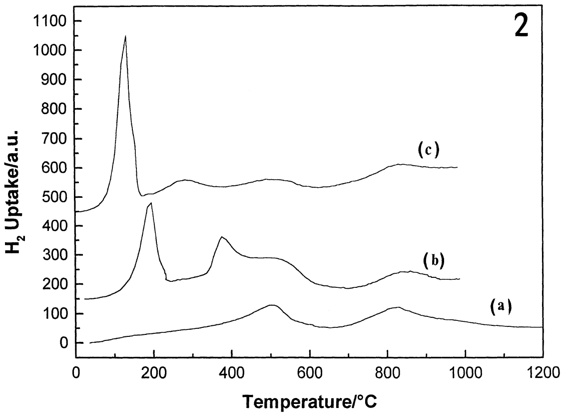

Fig. 2. H_2-TPR profiles obtained in standardised procedure from in situ preoxidised samples of: (1) CeO_2 (r.p.); (2) 0.5% RhO_x(ex.-acac.)//CeO_2(r.p.); (3) 4 wt.% RhO_x(ex.acac.)//CeO_2(r.p.).

ever, observed over the HTR-823 K sample during the initial 0.5 h contact with 5 mbar $^{15}N^{18}O$, (i) an approximately first-order decrease in $^{15}N^{18}O$ signal level resulting in 6.7×10^{19} fewer $^{15}N^{18}O$ molecules remaining in the gas phase over the HTR-823 K ceria sample after 0.5 h contact; (ii) initial signal level of $^{15}N_2$ was doubled relative to those in the other cases, and increased by a further 32% during the 0.5 h contact; (iii) $^{15}N_2{}^{18}O$, none of which had been detected over the preoxidised or LTR-423 K ceria, was initially detected in comparable amounts to the $^{15}N_2$ level and continued in parallel fashion with $^{15}N_2$ during the 0.5 h contact (cf. profiles in Fig. 1(B)). Those differences could be rationalised on the basis that HTR-823 K had greatly increased the concentration of oxygen anion vacancies in the ceria surface, thereby making available many more oxygen-accepting surface vacancy sites able to promote more dissociations via $^{15}N^{18}O_{(s)} + V_{ox} \rightarrow {}^{15}N_{(s)} + {}^{18}O_{(s)}$. Such $^{15}N_{(s)}$ fragments only could not only combine to yield $^{15}N_2$, but also diffuse and react with adsorbed $^{15}N^{18}O$ to yield $^{15}N_2{}^{18}O$. Conversely, some lessening of the probability for $^{15}N^{18}O \rightarrow {}^{15}N^{16}O$ exchange was to be expected over the HTR-823 K material, since prior HTR would have removed many of the low-coordinate, $^{16}O^{2-}_{(s)}$ or $^{16}OH^{-}_{(s)}$ required to drive exchange as per Eq. (1a) and Eq. (1b). This expectation was borne out by the much smaller number of $^{15}N^{16}O$ molecules (2.3×10^{19}) converted during the first 220°C rise in T-ramp from its onset over HTR-823 K CeO_2 than the 4.8×10^{19} molecules produced over LTR-423 K CeO_2 over the same range.

Preoxidised 0.5% RhO_x//CeO_2: Observations upon isotopic and other conversions of $^{15}N^{18}O$ over in situ preoxidised 0.5% RhO_x//CeO_2 were made in identical conditions to those noted above over CeO_2 alone. In view of the oxidising character of in situ preoxidation, and furthermore the oxidising character of the $^{15}N^{18}O$ probe gas, both the cerium and rhodium components could be considered to exist in oxidised form. Hence their designation by 0.5% RhO_x//CeO_2. On the basis of 66% dispersion measured for the 0.5% rhodium content, and a ceria surface area of 110 $m^2\ g^{-1}$, a ratio of 8.3:100 could be estimated between numbers of surface-exposed $^{16}O^{2-}_{(s)}$ related to rhodia and ceria, respectively. Despite this low fractional coverage of CeO_2 by RhO_x, the extent of $^{15}N^{18}O$ adsorption at r.t. was greatly enhanced, as evidenced by less than one-half of the introduced $^{15}N^{18}O$ remaining in the gas phase. Since no comparable effect had occurred over preoxidised CeO_2, such an enhanced uptake at r.t. could be attributed to the dispersed rhodia particles alone or in synergetic interaction with CeO_2. Fig. 3(A) shows that such an enhancement was not accompanied by detectable formation of $^{15}N_2$, or by increase of $^{15}N^{16}O$ above trace level: absence of $^{15}N_2$ product is again notable in Fig. 3(A) during T-ramp to 823 K when the sole changes observed in gas phase composition corresponded to thermally induced conversion of $^{15}N^{18}O$ to $^{15}N^{16}O$ with mirror-image relationship between the profiles for increase in $^{15}N^{16}O$ and decrease in $^{15}N^{18}O$. It thus appeared that oxidised sites containing RhO_x (possibly in synergetic interaction with CeO_2) strongly predominated not only in $^{15}N^{18}O$ adsorption at r.t., but also in directing conversion selectively towards $^{15}N^{16}O$ under thermal activation.

Over LTR 0.5% RhO//CeO_2: H_2-TPR profiles for preoxidised 0.5% RhO_x//CeO_2 (cf. profile *b* in Fig. 2) [15] have established the adequacy of exposure to H_2 at 425 K for complete reduction of the supported rhodia to metallic rhodium, and furthermore, shown that the spillover of hydrogen species occurs from the latter onto adjacent regions of the ceria, thereby partially reducing them at this relatively low temperature. Such were likely features of the material after LTR in H_2 at 423 K and before subsequent contact with 5 mbar $^{15}N^{18}O$ at r.t. Not surprisingly, new

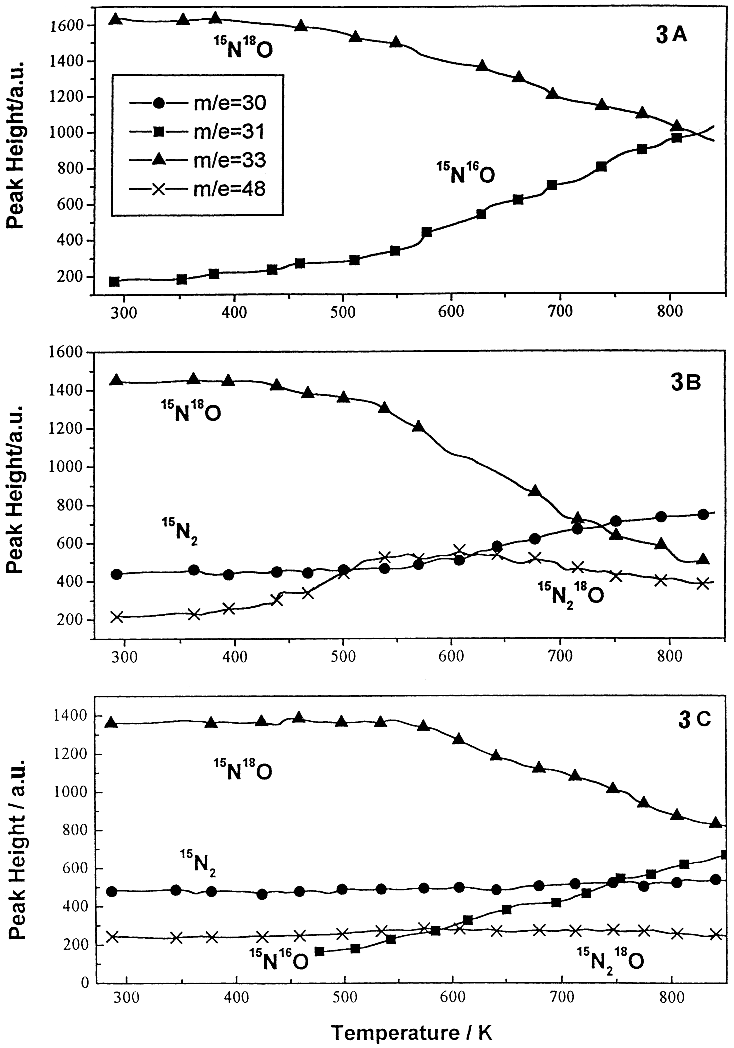

Fig. 3. (A) Composition of gas phase arising from r.t. contact of $^{15}N^{18}O$ with preoxidised 0.5% $RhO_x//CeO_2$ (data on l.h.s. of (A)), and profiles for TPR_x-induced changes under T-ramp at the rate of 10°C min^{-1}. (B) Data at equivalent stages after contact with a sample H_2-prereduced at 423 K. (C) Data at equivalent stages after contact with a sample H_2-prereduced at 823 K.

conversions, not witnessed at r.t. over preoxidised 0.5% $RhO_x//CeO_2$, then appeared (cf. Fig. 3(B)), including growth of $^{15}N_2$ during the first 10 min contact at r.t. to a constant limiting value equivalent to conversion of 35% of the introduced $^{15}N^{18}O$; plus presence of $^{15}N_2{}^{18}O$ equivalent to 7% conversion. These detections of enhanced $^{15}N_2$ and $^{15}N_2{}^{18}O$, albeit with moderate yields, pointed to the limited generation of ^{15}N-atom intermediates on the LTR-0.5% Rh^0/CeO_{2-x} surface and appeared consistent with literature reports of the ability of rhodium metal surfaces to dissociate nitric oxide at moderate temperatures, being thereby converted to $(RhO_x)_{(s)}$. Despite expectations that $RhO_x//CeO_2$ situations thus created might result in added activity via Eq. (1b), no increase in $^{15}N^{16}O$ was observed for the $^{15}N^{18}O//0.5\%$ $Rh^0//CeO_{2-x}$ system at r.t. or under T-ramp to 823 K. Small increases were observed in the yield of $^{15}N_2{}^{18}O$ up to 570 K and thereafter that of $^{15}N_2$ at 570→823 K (Fig. 3(B)). Failure to reproduce the $^{15}N^{18}O \rightarrow ^{15} N^{16}O$ activity seen over preoxidised 0.5% RhO_x//CeO_2 could, however, be rationalised on the basis that hydrogen spillover during LTR-423 K caused removal of most $^{16}O^{2-}_{(s)}$ or $^{16}OH^{-}_{(s)}$ from interfacial locations between ceria and $(Rh^0)_n$ particles. Consequently ^{15}N atom fragments formed on Rh^0 could not receive such species from ceria by reverse spillover, thereby limiting their fates to reaction with $^{15}N^{18}O$ to yield $^{15}N_2{}^{18}O$ or recombination to yield $^{15}N_2$.

$^{15}N^{18}O$ over HTR 0.5% RhO_x//CeO_2: Evidence for the more extensive removal of capping surface $^{16}O^{2-}_{(s)}$ of ceria by exposure to H_2 at 823 K than at 423 K deduced from TPR studies is illustrated in Fig. 2. An in situ reduction in H_2 at 823 K followed by evacuation yielded 0.5% Rh^0//CeO_{2-x} in such a condition before contact with 5 mbar $^{15}N^{18}O$ at r.t. Fig. 3(C) shows that the latter resulted in a moderate yield of $^{15}N_2$ and smaller yield of $^{15}N_2{}^{18}O$, both rather similar to those noted above from r.t. contact with this material after LTR-423 K. However, under T-ramp a greater rate of decrease in $^{15}N^{18}O$ became apparent above ~500 K, together with the somewhat unexpected reappearance of the isotopically exchanged species $^{15}N^{16}O$, which had not formed over this material after LTR-423 K. Progressive increases in $^{15}N^{16}O$ from 550 to 850 K were mirrored by decreases in $^{15}N^{18}O$ consistent with Eq. (1a) or Eq. (1b). Operation of that R_I-type process over HTR-0.5% Rh^0//CeO_{2-x} in that temperature range contrasted with its non-occurrence during a similar set of T-ramp observations upon that same material after LTR-423 K. That implied a reversal, in the HTR-823 K material, of the factor which had prevented R_1-type exchange in the LTR-423 K material, namely, inaccessibility in the latter of CeO_2-related $^{16}O^{2-}_{(s)}$ species for interaction with ^{15}N or $^{15}N^{18}O$ upon metallic rhodium particles. One plausible explanation for restoration of adjacent $^{16}O^{2-}_{(s)}$ anions of ceria in the HTR-823 K, but not in LTR-423 K 0.5% Rh^0//CeO_{2-x} would be if the HTR-823 K prereduction had sufficed to initiate the early stage of CeO_{2-x} migration onto the dispersed Rh^0 particles. HRTEM studies by Bernal et al. [16] have demonstrated that such migration, originating from large ceria crystallites, can result in complete encapsulation of sizeable Rh^0 particles after HTR-973 K and detectable coverage after HTR-873 K. Against that background, a lowering to HTR-823 K of the temperature adequate for initiating migration of CeO_{2-x} onto well-dispersed Rh^0 particles seems not improbable.

Experiments similar to those just described involving $^{15}N^{18}O$ in contact with 0.5% RhO_x//CeO_2 materials were made with unsupported Rh_2O_3 in the recirculatory reactor in *preoxidised* or in *LTR-423 K* condition. The barely detectable level of $^{15}N^{16}O$ over a preoxidised Rh_2O_3 sample, having many more Rh_2O_3 surface sites than number of dispersed RhO_x upon 0.5% RhO_x//CeO_2 material(s), argued against efficacy of Rh_2O_3 sites for $^{15}N^{18}O \rightarrow ^{15}N^{16}O$ conversions. However, after an in situ LTR-423 K pretreatment of the Rh_2O_3 (adequate for partial conversion to metallic rhodium), $^{15}N_2{}^{18}O$ again appeared in amounts as significant as from contact of $^{15}N^{18}O$ with 0.5% Rh^0//CeO_{2-x} in LTR-423 K condition. Support for a role for metallic rhodium in promoting $^{15}N_2{}^{18}O$ formation even in the absence of ceria is provided by this result.

3.2. Using equimolar $^{18}O_2 + ^{16}O_2$ as probe gas

Progress of isotope exchange processes having the following overall effect:

$$(^{18}O{-}^{18}O)_{(g)} + (^{16}O{-}^{16}O)_{(g)} \rightarrow {}^{18}O^{16}O_{(g)} + {}^{18}O^{16}O_{(g)} \qquad (2)$$

can be followed by MS. The term *homophase* is sometimes applied to such processes to acknowledge that such isotope-swops affect only gas phase composition. However, involvement of metal oxide surfaces in each of at least three-steps is essential: adsorption onto the promoting metal oxide; progress of isotopic swop between $^{18}O_{2(ads)}$ and $^{16}O_{2(ads)}$, occurring on special R_0-active sites; desorption of molecules isotopically distinguishable from the starting molecules. Successful outcome of such sequences is summarised by Eq. (2) and referred to as R_0-type oxygen isotope equilibration. Observations of the occurrence of the overall process over some metal oxide surfaces to temperatures as low as 200 K [11] imply that, in addition to the zero-enthalpy change for the overall process, $E_{(act)}$, the energies of each of the steps can be very low on favourable metal oxide surfaces. In the present work, room temperature (r.t.~295 K) was convenient to test for such low $E_{(act)}$, R_0-type activity of the different materials in preoxidised condition.

Constancy of AF18, the atom fraction of ^{18}O in the gas phase (whilst mole fractions of $^{18}O_2$, $^{16}O_2$ and $^{18}O^{16}O$ change), provides a valuable test for operation of R_o-activity only.

CeO_2(ex-nitrate): Introduction of an aliquot of "ex-nitrate" CeO_2 into the recirculatory reactor was followed by in situ calcination in 100 Torr $^{16}O_2$ at 823 K whilst maintaining recirculation through a liquid-N_2-cooled trap in the loop, prior to cooling to r.t. in that O_2, brief evacuation at r.t. and finally the introduction of 4 mbar of equimolar ($^{18}O_2 +^{16} O_2$). No alteration in isotopic composition of the latter occurred during r.t. contact for 1 h. Absence of any R_0-type activity was confirmed by an invariant value of AF18, the atom fraction of oxygen 18 in the gas phase. Fig. 4(A) summarises results obtained by MS-monitoring of isotopic composition of the recirculating gas phase whilst a T-ramp of 10°C min^{-1} was subsequently applied to the reactor segment. It shows that no evidence was found for any thermally activated, change up to 790 K, during which AF18 remained constant. The following changes were observed to onset at 800 K, and from 800 to 900 K to effect the following changes in the numbers of isomeric mole-

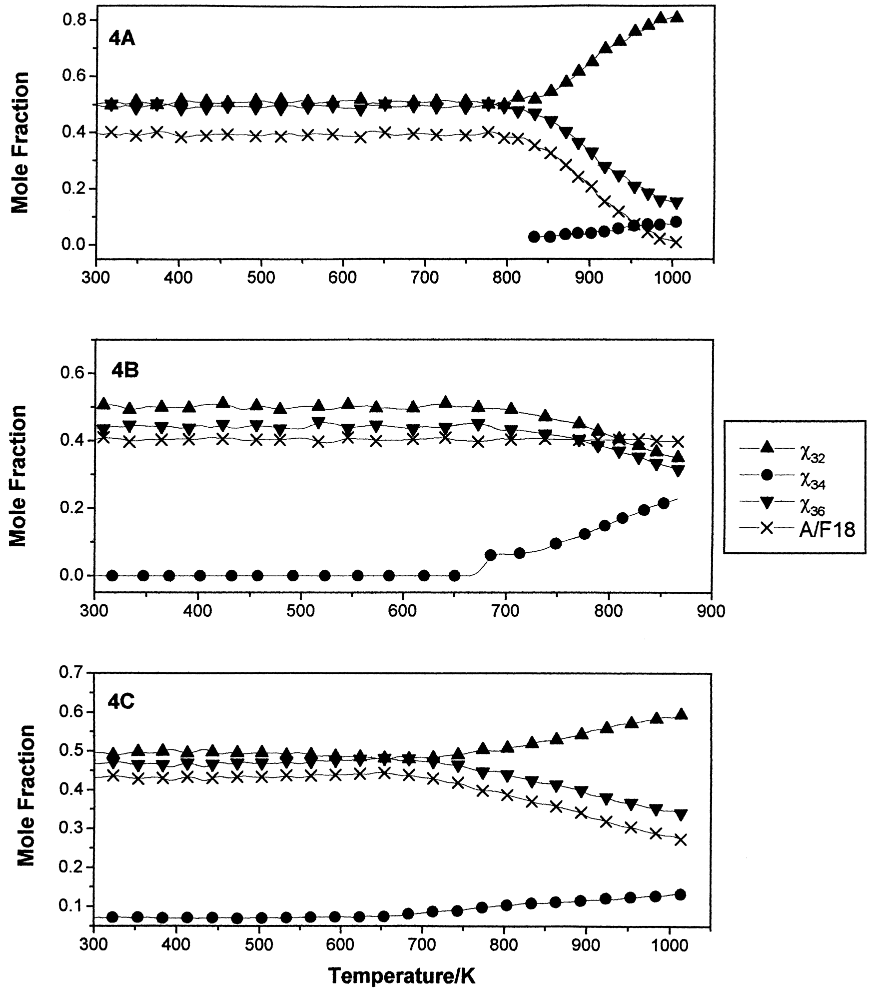

Fig. 4. (A) Changes in dioxygen gas phase composition arising from r.t. contact of equimolar ($^{18}O_2 +^{16} O_2$) with preoxidised CeO_2 (data on l.h.s. of (A)), and in profiles for TPR_x-induced changes under T-rampat the rate of 10°C min^{-1}. (B) Data at those stages after contact with preoxidised Rh_2O_3. (C) Data at those stages after contact with preoxidised 0.5% RhO_x//CeO_2.

cules in the gas phase: increase of $^{16}O_2$ by 1×10^{19}; decrease in $^{18}O_2$ by 1.2×10^{19}; and rather small increase of $^{18}O^{16}O$ by 2×10^{18}. Relative sizes of these changes appeared consistent with occurrence above 800 K of an 80%:20% mixture of the two possible heterophase oxygen isotope exchange processes, viz. double isotopic swops between $^{18}O_{2(ads)}$ with pairs of surface $^{16}O^{2-}_{(s)}$ species as per Eq. (3), termed R_2; and single isotopic swops with single $^{16}O^{2-}_{(s)}$ as per Eq. (4), termed R_1. Predominance of the R_2 process was also indicated by close similarity in the profiles for decreases in AF18 and $^{18}O_2$.

$$(R_2\text{-type})\quad (^{18}O^{18}O)_{2(g)} + (^{16}O^{2-}_{(s)}\ldots{}^{16}O^{2-}_{(s)}) \rightarrow{}^{16}O_{2(g)} + (^{18}O^{2-}_{(s)}\ldots{}^{18}O^{2-}_{(s)}) \qquad (3)$$

$$(R_1\text{-type})\quad (^{18}O^{18}O)_{2(g)} +{}^{16}O^{2-}_{(s)} \rightarrow{}^{18}O^{16}O_{(g)} +{}^{18}O^{2-}_{(s)} \qquad (4)$$

Since 800 K was also found to be the onset temperature for predominantly R_2-type exchange over preoxidised CeO_2 (r.p.), it appeared that the $\leq$0.4% La^{3+} content indicated in its specifications did not significantly influence R_2 or R_1 [13].

Rh_2O_3: In situ preoxidised Rh_2O_3 resembled preoxidised ceria in being wholly inactive for promotion of R_0-type activity at r.t. or under T-ramp up to 650 K. However, a marked difference from CeO_2 emerged at $T\geq663$ K, (cf. Fig. 4(B)) viz. onset of very effective promotion of R_0-type conversion of $^{18}O_2$ plus $^{16}O_2$ towards $2^{18}O^{16}O$ as per Eq. (2). The persistence of a constant value of AF18 up to 773 K not only confirmed the R_o-type character of the conversion, but also ruled out contributions in that temperature range by R_1 or R_2-type over fully preoxidised Rh_2O_3. However, mild in situ reduction of another preoxidised Rh_2O_3 sample by vacuum evacuation at 573 K, followed by cooling to r.t. in vacuo before introducing $(^{18}O_2 +{}^{16}O_2)$,brought about rather slow conversion of $(^{18}O_2 +{}^{16}O_2)$ to $^{18}O^{16}O$. That was reminiscent of earlier [21,22] reports that vacuum-outgassing at moderate temperatures generated R_0-type activity at r.t. in ZnO, TiO_2 and MgO powders which lacked such activity when preoxidised. An analagous interpretation thus seemed probable, viz. the creation of R_0-active oxygen anion vacancies on the Rh_2O_3 surface by vacuum-outgassing at 573 K. Other lines of evidence consistent with facile loss of O_2 from rhodia at moderate temperatures have come from O_2 (TPD) studies showing that preoxidised Rh_2O_3 yields a substantial O_2 (TPD) feature at 400 → 600 K [23] and furthermore that RhO_x dispersed on CeO_2 also yielded a smaller but measurable O_2 (TPD) feature in that range. Such observations were reconfirmed for the preoxidised RhO_x//CeO_2 materials used in the present study.

0.5% RhO_x//CeO_2(ex-nitrate): In line with above observations of zero change in $(^{18}O_2 +{}^{16}O_2)$ when contacted at r.t. with preoxidised CeO_2(ex-nitrate) or with Rh_2O_3 powder, no detectable change in isotopic composition or AF18 occurred during r.t. contact with 300 mg of this material. Such an absence of R_0-type activity at r.t. was also confirmed for analagous 0.5% PtO_x//CeO_2 and 0.5% PdO_x//CeO_2 materials. Effects subsequently observed over preoxidised 0.5% RhO_x// CeO_2 (ex-nitrate) under T-ramp from r.t. to 823 K diverged from what might have been expected from combination of the effects noted earlier for the Rh_2O_3 alone (solely R_0 at ~660 K) or CeO_2 alone (mainly R_2 at ~800 K). What developed instead over 0.5% RhO_x//CeO_2 (cf. Fig. 4(C)) was predominantly R_2-type activity onsetting at 673 K and evidencing: a progressive increase in $^{16}O_2$, a miror-image decrease in $^{18}O_2$ and accompanying progressive decrease in AF18. Some synergetic effects between the rhodia and ceria components was signalled by those observations. One such could involve reverse spillover of $^{16}O_2$ from ceria to rhodia locations capable of its facile release to the gas phase, whilst pairs of oxygen anion vacancies left behind on ceria component act to take up $^{18}O_2$ (or $^{16}O_2$) from the gas phase [24,25]. Results already mentioned concerning lower temperature for O_2-TPD features from RhO_x//CeO_2 than from CeO_2 [23] are consistent with that idea. Additional indirect support emerged from results of our comparisons between profiles for release of dioxygen product from N_2O dissociation over preoxidised 4% RhO_x//CeO_2 or over CeO_2 alone under T-ramp in the recirculatory reactor: over CeO_2 alone, N_2 was the only product released from N_2O decomposition up to 973 K, zero O_2 being detected: however, for $^{14}N_2{}^{18}O$ in contact with 4% RhO_x//CeO_2, $^{16}O^{18}O$, $^{18}O_2$ and $^{16}O_2$ species were already released to the gas phase at 450 K [22].

Other relevant questions were (i) whether the effective synergetic effect of wet-impregnated 0.5% RhO_x in lowering to 673 K the onset temperature for mainly

R_2-type exchange originated only from RhO_x species located in the surface region of microinterfaces on the 0.5% RhO_x//CeO_2(ex-nitrate), or (ii) might be contributed to by such species in sub-surface regions of the CeO_2 support. In our first attempt to address these questions, comparisons were made between T-ramp-induced changes in isotopic composition of 4 mbar aliquots of equimolar $(^{18}O_2 + ^{16}O_2)$ over (i) a sample of the usual ex-Rh(acac)$_3$ wet-impregnated 0.5% RhO_x//CeO_2(ex-nitrate) material; and (ii) those over a specially prepared 0.5% RhO_x//CeO_2(ex-nitrate) material obtained by *co-precipitation* of $Rh(NO_3)_3$ with $Ce(NO_3)_3$ followed by subsequent standard calcination and in situ treatments in $^{16}O_2$. Our expectation was that preparative method (ii) would mainly feature RhO_x species incorporated within the ceria particles, making them less effective. However the temperature for onset of R_2 activity of ~710 K over the co-precipitated material was only slightly higher than 673 K over the wet-impregnated sample. Furthermore, profiles for the progressive increases in $^{16}O_2$ and decreases in $^{18}O_2$ and in AF18, were rather similar to those described above for the corresponding material prepared by wet impregnation. Such lack of pronounced difference was unexpected.

Our second set of experiments addressing this question utilised 0.5% RhO_x//ZrO_2 prepared by wet impregnation with Rh(acac)$_3$, followed by standard calcination and in situ oxidation under $^{16}O_2$ at 823 K. Choice of such a material as the one yielding a strong probability of its rhodia content being predominantly concentrated on the ZrO_2 surface was influenced by recent reports by Burch et al. [26,27]. Their observation that severe preoxidation of such material did not bring about the severe degradation of catalytic activities widely reported for Rh/CeO_2 materials [5] led them to conclude that processes such as in-diffusion/burial of the rhodium content within ZrO_2 did not occur to significant extent for Rh/ZrO_2. On that basis it seemed reasonable to argue that any differences between 0.5% RhO_x//ZrO_2 and pure ZrO_2 in respect of T-ramp-induced R_2-type activity could be attributed to surface RhO_x species. Results from such an experimental comparison revealed that, ZrO_2 itself required T-ramp $\geq$873 K for onset and ongoing activity in which R_1>R_2, whereas the corresponding parameters over 0.5% RhO_x//ZrO_2 featured onset of activity at 748 K in which $R_2 \gg R_1$. Thus it could be concluded that sites featuring RhO_x species upon the surface of 0.5% RhO_x//ZrO_2 were primarily responsible for the change-over to predominantly R_2-type activity and for its incidence at onset temperature 125°C lower than that for the mainly R_1-type process over ZrO_2. Such RhO_x-containing surface locations upon 0.5% RhO_x//CeO_2 may likewise be important in effecting onset of R_2-type activity at lower temperature than over CeO_2. However, possibilities for promoting effects arising from sub-surface Rh^{n+} species may not be disregarded in that case.

4% RhO_x upon CeO_2 or Al_2O_3 or ZrO_2: A marked contrast was found between the above-noted absence of R_0-type activity at r.t. for CeO_2 wet-impregnated with 0.5% RhO_x, PtO_x, or PdO_x, when similar measurements were made upon CeO_2 (r.p.), prepared by wet impregnation with wet-impregnated with Rh(acac)$_3$ at 2% or 4%. Those latter evidenced such high R_0-type activity that $t_{0.33}$, the time required for 33% conversion to $^{16}O^{18}O$, was 45 or 20 min, respectively. The unchanging value of AF18 during such conversions pointed to the absence of any accompanying R_2 or R_1-type activity. Since preoxidised CeO_2 on its own had not shown any such R_0-activity, ceria regions of 2% or 4% RhO_x//CeO_2 surfaces unaffected by RhO_x could not be responsible for the R_0-type activity displayed by those materials. Emergence of substantial R_0-activity seemed rather to require the development of some RhO_x-related structural feature only established upon Ceria at such loadings. (A negative result consistent with this view emerged from absence of R_0-type conversion over 0.5% RhO_x//CeO_2 even after 10 h contact at r.t.). In the case of RhO_x dispersed upon preoxidised ZrO_2, similar evidence emerged for structure sensitivity of R_0-activity, viz. absence of detectable conversion of $(^{18}O_2 + ^{16}O_2)$ over 0.5% RhO_x//ZrO_2 whereas 33% conversion was attained in 42 min over 4% RhO_x//ZrO_2. A relative measure of the r.t. R_0-activity levels achieved as a result of dispersing 4% RhO_x(ex-Rh(acac)$_3$) upon the various metal oxide supports is provided by the following, bracketted $t_{0.33}$ values in min: /CeO_2 r.p.(2O); /Al_2O_3(38); /CeO_2–Al_2O_3(12); /ZrO_2(42). In addition to indicating the suitability of those supports 4% RhO_x-loaded supports for development thereon of the RhO_x-related structural feature required for substantial R_0-activity at 295 K, the variation within those $t_{0.33}$ values indicate that nature of the metal oxide support also exerts some influence. One likely source of such varying influence could come from the differing polarizing powers of the Ce^{4+}, Al^{3+} and Zr^{4+} support cations at contact perimeters with the active RhO_x structure. That would represent a *metal-oxide/metal-oxide* analogue of effects reviewed by Bell [28] for catalysis of structure-demanding conversions at contact perimeters in *metal-oxide/metal* systems.

Whenever wet impregnation with $RhCl_3$, rather than with $Rh(acac)_3$ was used as an alternative route to 4% RhO_x upon CeO_2 or ZrO_2, and those materials were preoxidised and then tested for R_0-activity in identical manner to that used for the ex-$Rh(acac)_3$ materials, no R_0-activity was found at 295 K. This striking inhibition of R_0-activity in the ex-$RhCl_3$ materials may be seen by comparing Fig. 5(B)(i) with Fig. 5(A)(i) for RhO_x//CeO_2, or Fig. 6(B)(i) with Fig. 6(A)(i) for RhO_x//ZrO_2. Within the context of the above-noted perimeter model, such total inhibition could be understood if ex-$RhCl_3$ chloride accumulated at such perimeters thereby disrupting adsorption and diffusion of $^{18}O_2$ and $^{16}O_2$ species thereon. Since dispersions of 33% and 30% were deduced for the rhodium content of ex-$Rh(acac)_3$ 4% RhO_x species upon CeO_2 and ZrO_2, whilst values for the corresponding ex-$RhCl_3$ materials were little different at 41% and 38%, explanation in terms of different dispersions seems less likely.

Arising from the above-noted operation of R_0-activity of the preoxidised, chloride-free 2% or 4% RhO_x//CeO_2 (r.p.) materials at r.t., isotopic composition of the gas after recirculation of the $(^{18}O_2 + ^{16}O_2)$ mixture over those samples for 1–3 h approached the mole fraction composition $\chi(^{18}O_2) : \chi(^{16}O_2) : \chi(^{18}O^{16}O) = 0.25 : 0.25 : 0.5O$ required by $^{18}O_{2(g)} + ^{16}O_{2(g)} \Leftrightarrow 2^{18}O^{16}O_{(g)}$ having

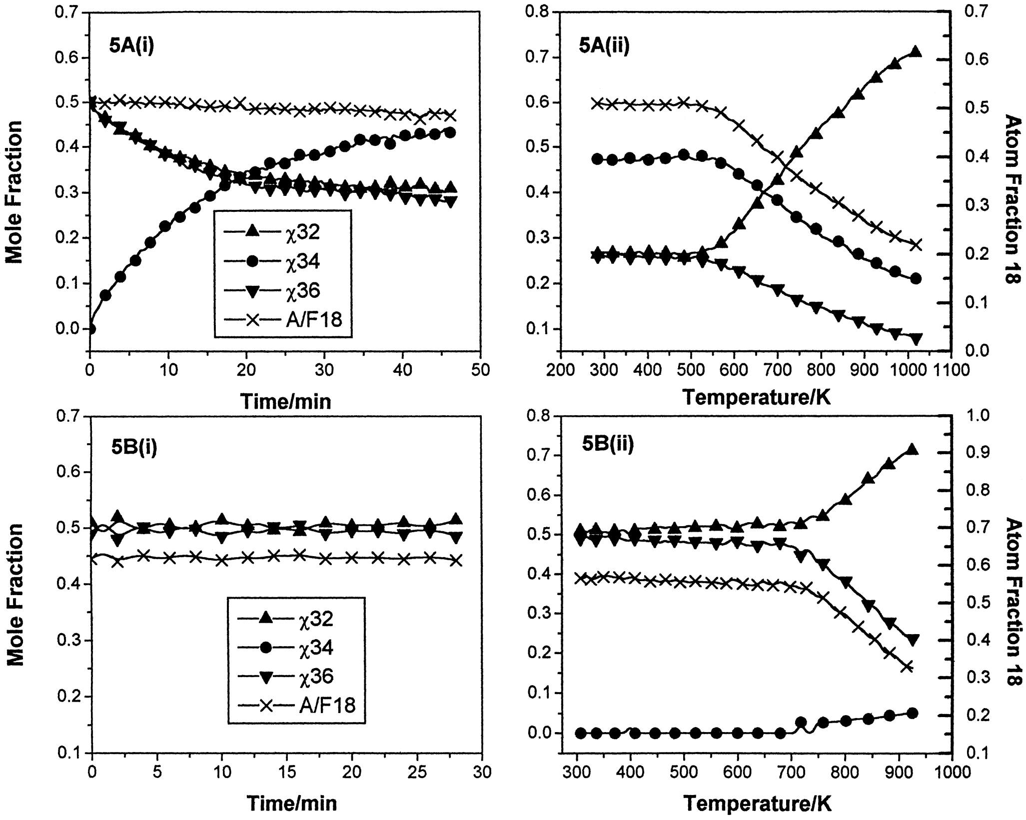

Fig. 5. (A) Changes in gas phase composition arising from contact of equimolar (O_2+O_2) with preoxidised, ex.$Rh(acac.)_3$, 4% RhO_x//CeO_2 at r.t. (A)(i) and under T-ramp (A)(ii). (B) (i) and (ii). Compositions at equivalent stages over preoxidised, ex-chloride 4% RhO_x//CeO_2.

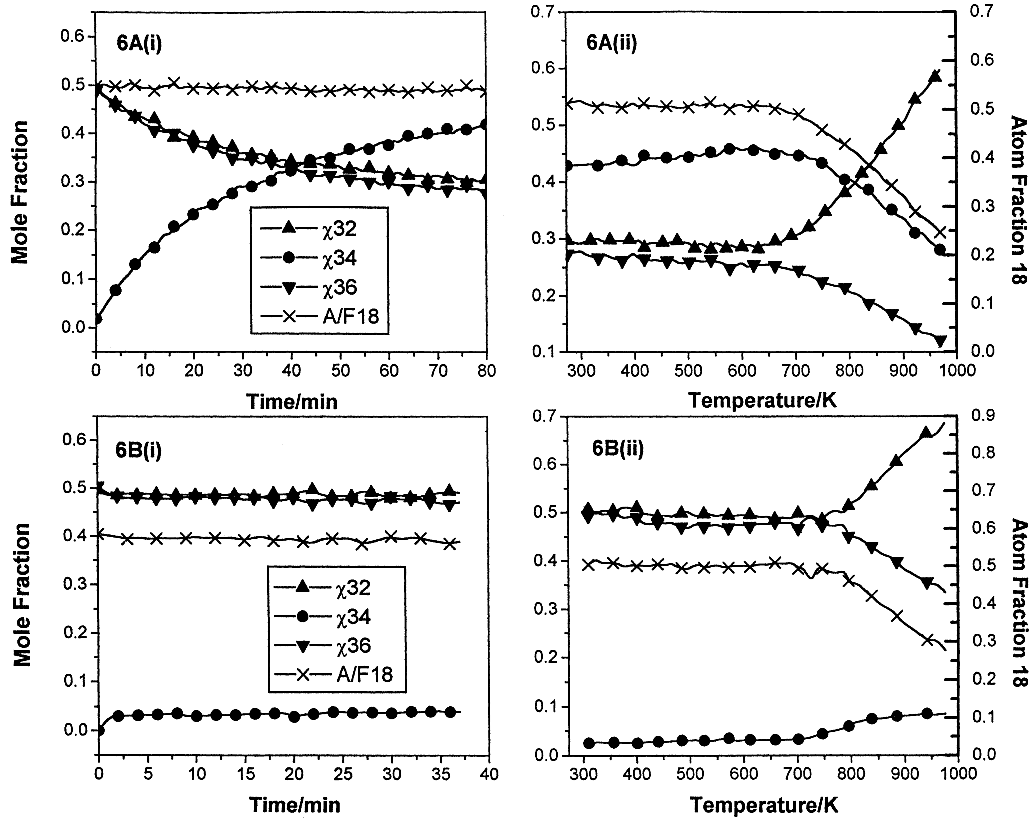

Fig. 6. (A) Changes in gas phase composition arising from contact of equimolar ($^{18}O_2$ +^{16} O_2) with preoxidised, ex-Rh(acac)$_3$ 4% RhO$_x$// ZrO$_2$ at r.t. (A)(i); and under T-ramp (A)(ii). (B)(i) and (ii), compositions at equivalent stages over preoxidised ex-chloride 4% Rho$_x$//ZrO$_2$.

K_{eq}=4.0. Fig. 5(A)(ii) illustrates profiles obtained for changes away from that composition upon applying a T-ramp and thereby bringing into operation thermally activated R_2- and/or R_1-type processes at ca. 573 K. Such profiles were more difficult to interpret than in cases such as Fig. 5(B)(ii) or Fig. 6(B)(ii) when no R_0-activity existed at r.t., one unknown being the extent to which R_0-activity observed at r.t. might remain effective at the higher temperatures and thus resist tendencies of any thermally induced R_1 and/or R_2-activities to drive isotopic composition of the gas phase away from that appropriate to R_0-equilibration. Procedures involving curve-fitting of isothermal kinetic data for changing oxygen isotopic composition of the gas phase over metal oxides have been utilised by various workers to deduce relative contributions by R_0, R_1 and R_2-type processes [29,30]. Being unable to identify corresponding analytical solutions for our situation where catalyst temperature was also varying under T-ramp, our assessment of the likely nature of the processes under T-ramp was limited to checks on the extent to which observed changes $+\Delta^{16}O_2$, $-\Delta^{18}O_2$ and $+\Delta^{16}O^{18}O$ across successive +25°C intervals above O.T. could be adequately accounted for on the basis of just one, or a combination of activities. These tests indicated that a satisfactory description of the experimentally observed profiles of $^{18}O_2$, $^{18}O^{16}O$ and $^{16}O_2$ versus ramp-temperature could be achieved on the basis that the predominant process occurring was of R_2-type, any contribution by R_1 and/or R_0 processes being less than one-fifth that of R_2.

Since dispersal of chloride-free 4% RhO$_x$ upon ceria had not only conferred r.t. R_0-activity, but also lowered by ca. 130°C the onset temperature for thermally activated R_2-activity, it was of interest to test whether ceria promoted by additions of oxides resembling rhodia might likewise enhance such activities. Praseodymium oxide was selected for experimental tests of such possibilities, largely on the basis of variable-valence capabilities similar to rhodia. Three mixed oxides of general formula $Ce_x\,Pr_{1\text{-}x}O_2$, having x=0.9, 0.7 or 0.5, were prepared by co-precipitation from mixed-nitrate, aqueous solutions as oxalates, followed by drying and calcination in O_2 at 923 K for 6 h. Tests for R_0-activity towards $(^{18}O_2 + ^{16}O_2)$ were made upon in situ preoxidised samples under standard conditions, but gave negative results for all $Ce_xPr_{1-x}\,O_2$ materials, not only at r.t., but also to 450 K under T-ramp (cf. data on l.h.s. axis of each section within Fig. 7). The contrast between such absence of measurable R_0-activity over the $Ce_xPr_{1-x}O_2$ at r.t., versus the substantial R_0-activity described above for 4% RhO_x//CeO_2 or its coprecipitated equivalent $Ce_{0.96}Rh_{0.04}O_2$, indicated once again the special role of rhodia at ≥4% upon/in ceria in promoting R_0-activity. Incorporation of lantana in ceria was previously shown ineffective in promoting such R_0-activity [13].

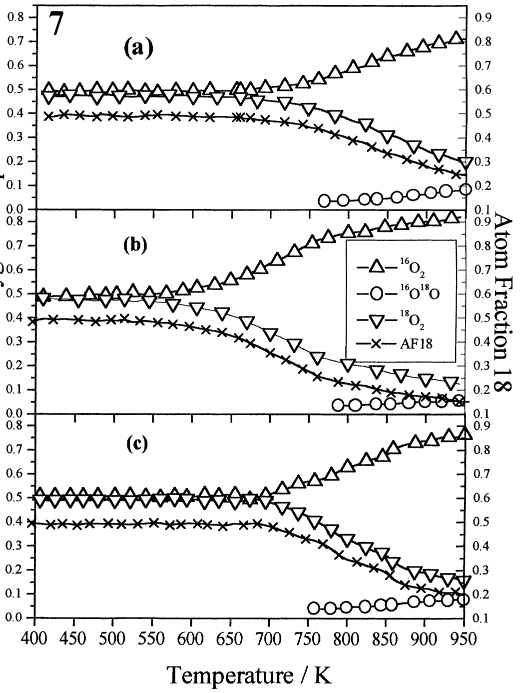

Fig. 7. Changes in gas phase composition arising from contact of equimolar $(^{18}O_2 + ^{16}O_2)$ with preoxidised $CeO_xPr_{1-x}O_2$ under TPR_x upward from 400 K. Plot (a), (b) and (c) over materials containing 10%, 50% and 100% PrO_2 , respectively.

Comparisons between the profiles in Fig. 7(A)–(C) do, however, show that incorporation of increasing amounts of PrO_x into CeO_2 caused the onset temperature for predominantly R_2-type exchange to move downward from 800 K for CeO_2 (not shown) to 675 K with 10% PrO_x, 650 K with 30% PrO_x and to 575 K with 50% PrO_x. Also indicative of an increase in predominantly R_2-activity with increasing content at PrO_x was the progressive increase in magnitude of the difference (χ_{32}–χ_{36}) achieved at 950 K – viz. 0.52, 0.63, and 0.70, respectively. Support for exclusively R_2-activity in these materials at ramp temperature within 100° of their onset temperatures comes from (i) the manner in which the profile for decreasing χ_{36} is tracked by that for AF18 and (ii) the barely detectable $^{18}O^{16}O$ signal up to 575 K before subsequent slight increase.

4. Conclusions

(A) The lower overall dispersions of ca. 40% deduced for rhodia species upon preoxidised RhO_x// CeO_2 or RhO_2//ZrO_2 having 4% or 2.1% rhodia loadings, relative to 66% for those with just 0.5% RhO_x loading, established the existence of larger rhodia particles on the former. Thus a feasible conclusion from the contrasting observations of high R_0-type activities of chloride-free, preoxidised 4% RhO_x// CeO_2 and 4% RhO_x//ZrO_2 materials at 295 K versus absence of any such activity over 0.5% RhO_x//ZrO_2 or 4% RhO_x//CeO_2 in similar conditions, is that this isotopic equilibration processes at 295 K was structure-demanding in respect of efficiency of the *rhodia-component* dispersed thereon. Another aspect of present results consistent with a central role of rhodia in R_0-activity was that unsupported preoxidised Rh_2O_3 was the sole pure preoxidised metal oxide powder found to exhibit such activity, albeit at >663 K. Present results do not permit definitive identifications of the nature or mode of operation of sites involving larger rhodia particles which give rise to R_0-activity by chloride-free 4% RhO_x//CeO_2 and //ZrO_2. Availability of ordered arrays of Rh^{n+}-containing sites capable of dioxygen adsorption and diffusion thereon – e.g. at contact perimeters between larger rhodia particles and metal oxide support – represents a more probable origin of such activity than literature models associating such R_0-activity on TiO_2 or ZnO with oxygen anion vacancies.

(B) The following general features emerged from our analyses of profiles versus T-ramp for changes in isotopic composition of $(^{18}O_2 + ^{16}O_2)$ probe gas over $RhO_x//CeO_2$ at moderate temperatures: (i) progressively lower onset temperatures observed with increasing contents of rhodia and (ii) strong predominance of R_2-type heterophase oxygen isotope exchange with pairs of lattice $^{16}O^{2-}_{(s)}$ evidenced at temperatures within 100° of onset. Feature (i) points to a role of rhodia in facilitating the release of $^{16}O_2$ into the gas phase, leaving behind pairs of oxygen anion vacancies upon surfaces of the binary metal oxide support. Feature (ii) may be understood within the context that uptake of $^{18}O_{2(g)}$ by these pairs of oxygen anion vacancies complements feature (i) giving the net R_2-type overall effect of loss of one $^{18}O_2$ from the gas phase and release thereto of one $^{16}O_2$. On the basis of his extensive studies of thermally activated oxygen isotope exchange over single-component metal oxides, Winter included ceria into one group showing mainly R_2-type activity and identifed ease-of-self-dissociation as a common factor [7,8]. Results from recent studies of O_2 release from ceria films under T-ramp [31] identified a very similar onset temperature to that here observed for R_2-type activity. Present observations are consistent with that result and Winter's idea and extend the latter to include the promoting effect of certain second-component metal oxides in ceria-based, binary metal oxide systems. The well-known capabilities of ceria for spillover of oxygen in the reverse or forward directions undoubtedly also contribute to present observations [5,6,24,25].

(C) Observations upon T-ramp-induced alterations in the isotopic composition of the doubly labelled $^{15}N^{18}O$ probe gas over preoxidised CeO_2 or 0.5% $RhO_x//CeO_2$ indicated $^{15}N^{18}O_{(g)} + ^{16}O^{-2}_{(s)} \rightarrow ^{15}N^{16}O_{(g)} + ^{18}O^{2-}_{(s)}$ to be the dominant overall effect of heterophase oxygen isotope exchange over both materials above ca. 450 K. Possible contributions by analagous exchange events involving surface $^{16}OH^{-}_{(s)}$ rather than $^{16}O^{2-}_{(s)}$ cannot be excluded on the basis of present results. These are formally R_1 in character, the appearance and progressive growth of which over these $^{15}N^{18}O/MO$ interfaces at $\geq$450 K contrasts markedly with failure of $(^{18}O_2 + ^{16}O_2)$ probe gas to undergo analagous R_1-type heterophase oxygen isotope exchange over CeO_2 and $RhO_x//CeO_2$ at similar temperatures. In the case of 0.5% $RhO_x//CeO_2$ where evidence was found for extensive adsorption of $^{15}N^{18}O$, efficient scavenging by such $^{15}N^{18}O_{(ads)}$ of any surface lattice anionic species could be responsible for the absence of R_2-activity and for non-appearance of $^{16}O_2$ product in the gas phase. Species formed as surface-intermediates via such scavenging represent the probable source of $^{15}N^{16}O$ product seen to increase in the gas phase under T-ramp.

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