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Contrasting dynamic responses of supported Rh nanoparticles to H_2S and SO_2 and subsequent poisoning of NO reduction by H_2†

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H_2S induces rapid sulfidation of the Rh nanoparticles at room temperature and completely poisons NO reduction by H_2; SO_2 elicits an equally rapid but subtle modification of nanoparticle structure but has little effect upon NO reduction at 523 K.

The structural response of supported nanoparticles to the adsorption of gaseous species is of intrinsic interest to wide range of applications. Sulfur containing molecules can be extremely efficient poisons in many catalytic processes including the reduction of NO by Rh based systems.[1] Equally, however, sulfur can positively affect selectivity in others.[2]

The structural ramifications of the adsorption of sulfur containing molecules upon Rh has generally been the focus of studies based upon extended single crystal surfaces[3] rather than model or supported nanoparticles which, in other cases, are known to respond morphologically to sulfur adsorption[4]

Using energy dispersive EXAFS (EDE), we have recently shown that exothermic dissociative adsorption of NO can induce even more radical change (rapid oxidation at room temperature) in supported Rh nanoparticles.[5] The reversal of this oxidation is a key limiting factor in determining reaction light off and N_2O production during NO reduction by H_2 over Rh catalysts.[6]

Many other gases have the potential to elicit such change, given rapid dissociation and the strong adsorption of at least one of the molecular components. Both H_2S and SO_2 fall into this category and as such we have investigated how γ-Al_2O_3 supported Rh particles respond to these gases and how these responses affect NO reduction by H_2.

Rh K edge (EDE) measurements were made at ID24 of the ESRF using an asymmetrically cut Si[111] monochromator in a Laue configuration.[7] Detection was made using a Peltier cooled, phosphor-masked, CCD detector.

5wt% Rh/γAl_2O_3 samples were prepared by wet impregnation of $RhCl_3{\cdot}3H_2O$, drying, followed by calcination at 673 K for 5 h and subsequent reduction at 573 K for 6 h. 20 mg was loaded into a custom built microreactor[8] and re-reduced at room temperature under 10 ml min^{-1} 5% H_2/He prior to purging with He and exposure to reactive gas mixtures. Sample temperature was measured *via* a type k thermocouple inserted directly into the packed catalyst bed. EXAFS was carried out using PAXAS[9] and EXCURV98.[10]

Fig. 1 shows mass spectrometric (*m*/*z* 34 (H_2S) and *m*/*z* 64 (SO_2)) and thermal data obtained at the same time as EDE measurements during room temperature exposure of the Rh samples to 5%H_2S/He and 5%SO_2/He. Both gases are instantly taken up at room temperature and this adsorption is accompanied by very similar ~6 K exotherms. In the case of H_2S a burst of H_2 accompanies the exotherm and is the only significant desorption event observed in either case. Superficially, therefore both gases elicit a very similar thermal response in the catalyst bed. Calculation of the measurable uptake of each gas reveals that much more SO_2 (3.8(±0.1) SO_2/Rh) is adsorbed by the sample than H_2S (~ 0.63(±0.1) S/Rh).

Fig. 2a and b shows the structural response of the supported Rh particles during the switch a He flow to 5% H_2S and 5% SO_2 in He. In each case, data pertaining to Rh–Rh and Rh–S co-ordination, along with Rh–Rh bond length variation is shown. Representative k^3 weighted EDE data are given as ESI.†

These experiments show that, though the interaction of both sulfur containing species with the supported Rh is very rapid, the structural response induced in the Rh nanoparticles is different in each case. H_2S induces a very rapid sufidation (< 5 s) followed by a slower process that eventually results in formation of a nanoparticulate RhS (2.71 < Rh–Rh < 2.72 Å, Rh–S = 2.3 Å) after *ca.* 2 minutes of exposure to H_2S. This character is deemed most likely to result from an initial sulfidation of the surface region of the particles followed by slower sulfidation of the remaining Rh core. However, we cannot rule out this character being due to differential rates of sulfidation occuring for differing sized particles within the Rh particle size distribution.

The Rh–S distance is consistent with for bulk Rh sulfides by X-ray diffraction.[11] However, the Rh–Rh is significantly shorter than expected for Rh_2S_3,[11b] though Rh–Rh bond lengths of this magnitude have been reported for Rh_3S_4[11a] and $Rh_{17}S_{15}$.[11c] These data also indicate an average Rh–S–Rh bond angle of only *ca.* 73°. The closest bulk analogue to this species, both structurally and stoichiometrically is $Rh_{17}S_{15}$.[11c] However there is no clear bulk analogue of this nano-sulfide. We may

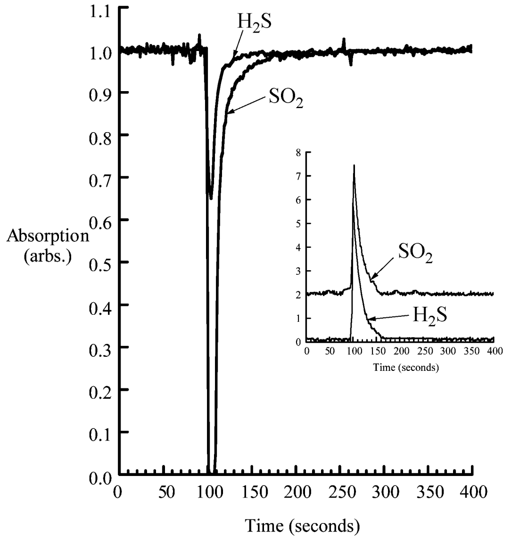

Fig. 1 Mass spectrometric and thermal (inset) responses derived from exposure of reduced 5 wt% Rh/Al_2O_3 to 10 ml min^{-1} 5% H_2S/He (*m*/*z* = 34) and to 20 ml min^{-1} 5% SO_2/He (*m*/*z* = 64).

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† Electronic supplementary information (ESI) available: EDE spectra. See http://www.rsc.org/suppdata/cc/b3/b304001a/

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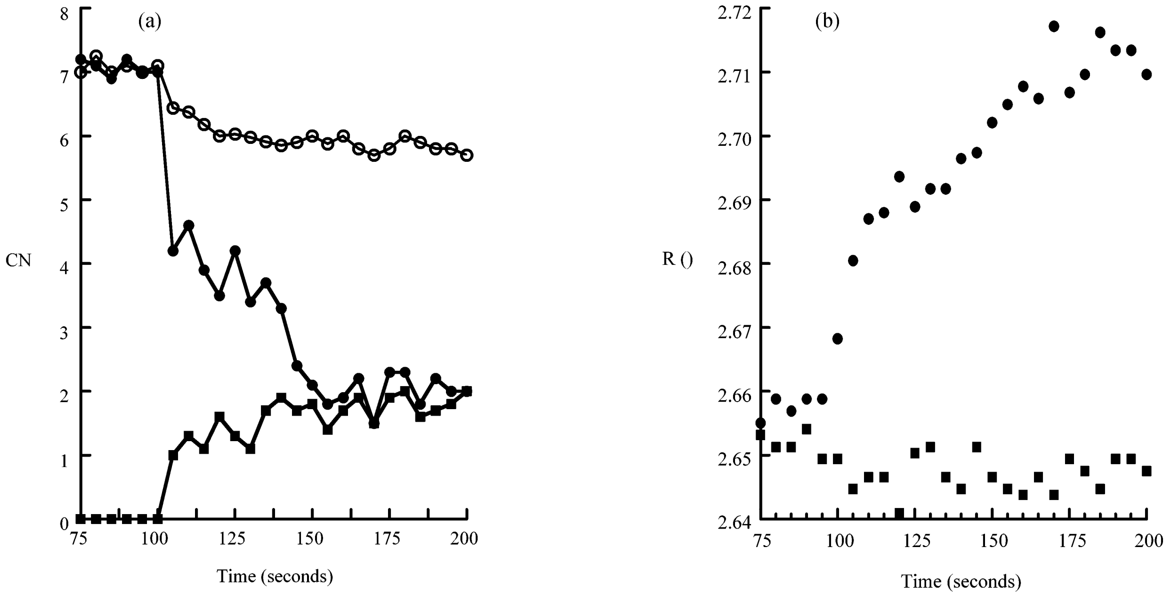

Fig. 2 (a) Temporal variance in Rh co-ordination (CN) derived from the EDE data during gas switches from He to 5% H_2S/He and 5% SO_2/He. Filled circles = Rh–Rh (H_2S); open circles = Rh–Rh (SO_2); squares = Rh–S (H_2S). No significant low O or S co-ordination was observed to evolve during SO_2 exposure. (b) Temporal variance in Rh–Rh nearest neighbour bond lengths during gas switches from He to 5% H_2S/He (circles) and 5% SO_2/He (squares).

conclude, however, that the shortened Rh–Rh distance and acute Rh–S–Rh bond angle result from constraint to three dimensional nanoscale domains (no significant additional Rh–O co-ordination results from H_2S adsorption, as might be expected if the sulfide wets the Al_2O_3 support).

The sulfide is stable to temperatures in excess of 673K under flowing H_2/He and the *in situ* sulfiding of such a system catalysing NO reduction in H_2 ($H_2 : NO = 1.5$) at 525 K results in a complete curtailment of activity (from $>90\%$ NO conversion with practically no N_2O production).[9]

Despite eliciting a similar thermal response from the catalyst bed, SO_2 exhibits a very different structural response from the supported Rh nanoparticles. Though the change observed is just as rapid, no evidence for oxidation or sulfidation is found at 300 or 373 K; indeed, despite the high level of SO_2 uptake, no significant O or S contributions are observed in the EXAFS. Instead only a small decrease in the apparent Rh–Rh co-ordination number (from ca 7.2 to 5.7) is indicated. Though subtle this change is clearly observed in the raw absorption data (see ESI†). Such a variation in first shell Rh–Rh co-ordination would point to an approximate halving (from *ca.* 50 to 25 atoms[12]) of the average particle size, though a more complex morphological variation cannot be ruled out. This, however, is in significant contrast to the promotion of Pt particle sintering in Pt/Al_2O_3 catalysts by the same gas.[13]

In complete contrast to the highly deleterious effect of H_2S on NO reduction by H_2, the repeated pulsing of 5% SO_2/He into a 10 ml min^{-1} flow of NO/H_2/He ($H_2 : NO = 1.5$) over a period of *ca.* 20 min produces no significant effect on this reaction at 523 K with net NO conversion remaining at the 90% level.

In summary these data show that, though the potential for exothermic dissociation of SO_2 exists, it is not realised on small Rh nanoparticles. The interaction of SO_2 with the catalyst is primarily molecular and predominantly occurs on the support resulting in a total SO_2 uptake of *ca.* 11 SO_2 nm^{-2} at room temperature. A subtle modification in the structure of the supported Rh, is observed, however, it is of little consequence to the NO/H_2 reaction on the timescales investigated ($<$ 30 min). In stark contrast, the exposure of Rh nanoparticles to H_2S results in the highly exothermic dissociative adsorption and the irreversible formation of nanoscale H_2S. The formation of this new phase results in the swift and long lasting poisoning of NO reduction by H_2 by the supported Rh catalyst.

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