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Synchronous, time resolved, diffuse reflectance FT-IR, energy dispersive EXAFS (EDE) and mass spectrometric investigation of the behaviour of Rh catalysts during NO reduction by CO†

Mark A. Newton,*[a] Bhrat Jyoti,[a] Andrew J. Dent,[b] Steven G. Fiddy[c] and John Evans*[a,b]
[a] *School of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ.*
E-mail: m.a.newton@soton.ac.uk; je@soton.ac.uk; Fax: + 44 (0)2380 593781;
Tel: + 44 (0)2380 596744
[b] *Diamond Light Source, Chilton, Oxford, UK*
[c] *The European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, Cedex 9, France*

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Synchronous, time resolved, infra-red, XAFS, and mass spectroscopies are simultaneously applied *in situ* to the investigation of the dynamic behaviour of Rh/Al_2O_3 catalysts during NO reduction by CO; NO conversion, and its kinetic character are closely correlated to the conversion of Rh(I) (predominantly $Rh^I(CO)_2$) to Rh(0).

In a wide range of disciplines understanding the overall behaviour of complex chemical systems requires the investigation of a combination of parameters. A battery of techniques has been developed to determine the net performance for a given process, the structure of the active phase, and the species interacting at the surface of the support/active phase. Ideally all these probes would be brought to bear on a chemical system in an *in situ* manner, and in a single experiment. In this communication we combine three temporally resolved, and complementary spectroscopies, to uniquely permit this to be done. As an exemplar we apply this new approach to understanding the structuro-reactive development of two supported Rh catalysts as they evolve as a function of temperature to catalyse NO reduction by CO.

Experiments were conducted on ID 24 at the ESRF. Dispersive EXAFS (EDE) measurements were carried out at the Rh K edge using an asymmetrically cut (10°) Si[111] polychromator mounted in a Laue configuration,[1] and a Peltier cooled, phosphor masked, CCD camera (Princeton) for detection. Due to detector readout limitations a total acquisition time of between 1.2 and 1.5 s per EDE spectrum yielded *ca.* 10 spectra min^{-1} and 1 spectrum K^{-1}, given the experimental heating rate (10 K min^{-1}). Diffuse reflectance infra-red measurements were obtained in a geometry orthogonal to the EDE data using a BioRad FTS 7000 IR spectrometer and a linearised, high sensitivity MCT detector. The unpressed powder sample (*ca.* 40–50 mg, 100 μm sieve fraction; calcination and reduction procedures have been previously reported[2–3]) was mounted within a custom built DRIFTS cell† and contained within a pyrolytic boron nitride (BN) mount (5 mm id, 3 mm depth, 0.06 cm^3) to permit transmission of X-rays through the sample. In addition the cell was X-ray windowed with hot pressed BN and IR windowed with 2 mm thick CaF_2 or ZnSe. EDE measurements were made within the top 0.5–1 mm of the sample bed. This custom cell was mounted with a standard DRIFTS optics (Spectratech). To match the EDE acquisition rate a time resolution of 6 s was used for DRIFTS measurements. This cell arrangement also allowed for the switching of gas feeds into the cell under mass flow control (in this case 50 ml min^{-1} total flow of a 5% CO in He and 5% NO in He to yield a CO:NO ratio of 1) and heating of the sample to a current limit of *ca.* 600 K. Downstream analysis of the feedstock composition was monitored continuously using a mass spectrometer (Pfeiffer) and a stainless steel sampling capillary. EXAFS data reduction and analysis were carried out using PAXAS[4] and EXCURVE98.[5] Prior to reaction with the He/CO/NO feedstock samples were reduced in flowing 5% H_2/He at 573 K.‡

Fig. 1 shows raw Rh K edge EDE data obtained between 300 and 573 K during heating of a 5wt% $Rh(NO_3)_3$ derived, γ-Al_2O_3

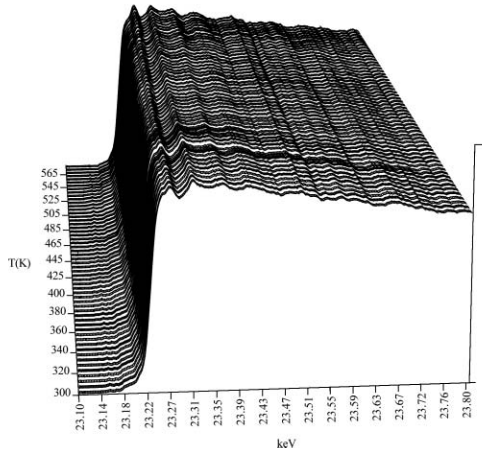

Fig. 1 Rh K edge EDE of 5 wt% Rh/Al_2O_3 {ex $Rh(NO_3)_3$} as a function of temperature during NO reduction by CO. One spectrum every 5 K is displayed.

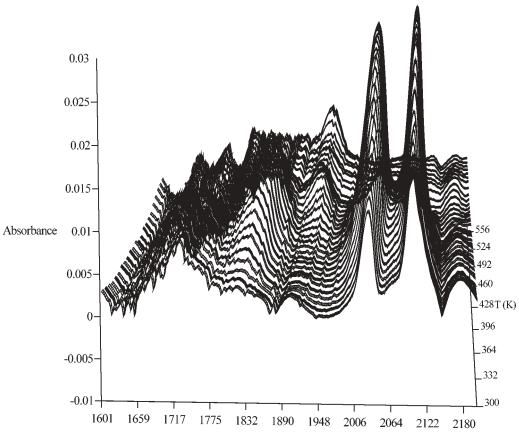

Fig. 2 Diffuse reflectance infra-red spectra (1600–2200 cm^{-1}; 4 cm^{-1} resolution) obtained synchronously with the EDE data shown in Fig. 1. For clarity one spectrum per 8 K is shown.

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† Electronic supplementary information (ESI) available: Overview of proposed combined DRIFTS/Energy Dispersive EXAFS cell. See http://www.rsc.org/suppdata/cc/b4/b405694a/

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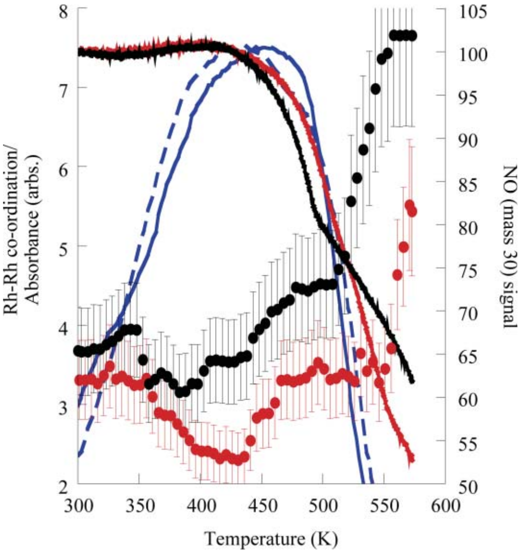

Fig. 3 Variation in Rh–Rh co-ordination (filled circles), net NO signal (—), during NO reduction by CO over chlorinated (red) and non-chlorinated (black) Rh/Al_2O_3 catalysts. The intensity of the asymmetric stretch of the $Rh^I(CO)_2$ species (dashed blue for the chlorinated case) is also shown. Error bars on Rh–Rh co-ordination are shown at ±15%.

supported catalyst under the He/CO/NO feedstock. Fig. 2 shows the corresponding synchronously obtained DRIFTS data.

From this data, in particular the structure of the near edge region, there is very little evidence for Rh being present in a +3 oxidation state at ambient temperature and above, in stark contrast to the behaviour observed during NO reduction by H_2.[3] It is also clear from the IR data that there is little indication of the presence of adsorbed CO species that would be associated with extended Rh surfaces (for instance linear and bridging CO species).[6] Indeed over the temperature range indicated the only carbonyl species observed is the $Rh^I(CO)_2$ centre. The nitrosyl region of the IR spectra point to a range of species {for instance $Rh(NO)^+$, $Rh(NO)_2$, $Rh(NO)^-$}[7–10] all of which display different temperature dependencies, though the behaviour of the $Rh(NO)_2$ bands mirrors that of the $Rh^I(CO)_2$ species.

Fig. 3 compares the average Rh–Rh co-ordination obtained from analysis of the EDE spectra to the net NO residue (%) observed during NO reduction over $RhCl_3$ and $Rh(NO_3)_3$ derived catalysts and also shows the variation in the intensity of the asymmetric stretch of the $Rh^I(CO)_2$ species formed in each case.

From these data we can see that the onset and kinetic character of NO conversion are highly correlated to the structure of the Rh phase. This is especially clear in the behaviour of the nitrate derived system where, although NO conversion is observed before the appearance of a clearly metallic Rh phase, a change in kinetic character of this conversion (*ca.* 500 K) may be directly associated with the formation of "metallic" Rh. This reduction of the Rh phase does not occur until $T > 550$ K in the case of the chlorinated precursor. Because of this, and the modification in kinetics that this structural change creates, the net NO conversion from the chlorinated system is close to 10% better than that achieved from the nitrate derived system despite the latter system showing a slightly lower light off temperature. In both cases, significant NO turnover is observed in the absence of a Rh phase that may be associated with extended Rh surfaces.

The predominance of $Rh(CO)_2$ centres in the carbonyl region of the infra-red spectrum below 500 K is entirely consistent with the low level of Rh–Rh co-ordination observed from the EDE and from simple inspection of the shape of the XANES region. However, this in itself is not expected on the basis of previous studies of similar systems exposed to CO alone.[11,12] Those studies found $Rh(CO)_2$ to be formed significantly only for Rh particles displaying a Rh–Rh co-ordination of <4–5. In contrast, after initial reduction, our samples show Rh–Rh co-ordination of *ca.* 8. From this we might conclude that the addition of an easily dissociable oxidant such as NO promotes the formation of species such as $Rh^I(CO)_2$. NO evidently does oxidise the metallic centres more readily than CO, but these are only converted into the $Rh(CO)_2$ sites above 300 K. There is no evidence that, once formed, the $Rh^I(CO)_2$ species is actively stabilised through the presence of chlorine in the catalyst make up, as has also been previously suggested.[13] The same is true of bands associable with $Rh(NO)_2$ sites.[8]

These data also show that the use of a chlorinated precursor staves off the formation of a clearly metallic phase relative to its chlorine free counterpart. In the latter case it is possible to associate the formation of metallic Rh with the removal of the $Rh^I(CO)_2$ species. For the chlorinated samples, though the $Rh^I(CO)_2$ sites decline in the same manner, there is no evidence of a significant reduction of the Rh phase until $T > 550$ K (where the $Rh^I(CO)_2$ has attenuated to <1/8th of its maximal intensity); as such these experiments do provide direct evidence for Cl stabilising Rh in an oxidation state higher than 0 but not for this remaining to be $Rh^I(CO)_2$ (or indeed, $Rh(NO)_2$). $Rh(NO)^+$ sites (at. $\sim 1920\ cm^{-1}$) are also seen to be evolved above 500 K.

In summary we have successfully combined three complementary spectroscopies in a truly *in situ* synchronous and time resolved manner. These three spectroscopies permit us to simultaneously interrogate catalyst activity, local structure, and surface speciation. As such a highly detailed window into the structure function relationships at work in such catalytic systems may be obtained.

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Notes and references

‡ After reduction in 5% H_2/He at room temperature EXAFS showed Rh–Rh co-ordinations of 8 for both chloride and nitrate samples. TEM of the "fresh" oxidic samples[2,3] yielded mean particle diameters of 2.15 nm (SD = 0.5 nm chloride) and 2.6 nm (SD = 0.7 nm – nitrate). As such the particle size distributions derived in each case were very similar. XPS indicates that after calcinations and reduction the $RhCl_3$ derived catalyst retains Cl to the level of Rh:Cl = 1:1.8.

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