DOI: 10.1002/anie.200701419

Catalyst Structure

Rhodium Dispersion during NO/CO Conversions**

Andrew J. Dent, John Evans, Steven G. Fiddy, Bhrat Jyoti, Mark A. Newton, and Moniek Tromp*

The catalyzed reaction between NO and CO for NO_x removal is a key component of the role of rhodium in automotive exhaust catalysts.[1] Kinetic models for this reaction have been reported[2] with structural inferences based on Rh(111). Surface-science studies have provided elegant descriptions of surface oxidation (by O_2).[3] However, the mean nuclearity of the metal on Rh/Al_2O_3 during the reduction of NO by H_2 varies with gas partial pressures and temperature.[4] Hence, an assumption of an invariant core catalyst may be invalid for highly dispersed catalysts. Indeed, combinations of CO and NO at low temperatures (< 473 K) aggressively corrode nanoparticulate rhodium to release $Rh(CO)_2$ centers,[5] which are mononuclear[6] and whose generation has also been monitored kinetically.[7]

Our previous experiments showed that 5 wt% Rh/Al_2O_3, prepared from rhodium trichloride, underwent structural changes during a thermal ramp under a 1:1 mixture of 5% CO/He and 5% NO/He.[5] At room temperature, the predominant IR bands for the adsorbates were owing to $Rh^I(CO)_2$ units and the mean Rh–Rh coordination number was found to be approximately 3. By 473 K, the intensity of the $\nu(CO)_{as}$ IR band (as = asymmetric) owing to $Rh(CO)_2$ centers was just past its maximum.

In this study, the simultaneous monitoring of catalysts by diffuse reflectance and time dependence of any structural changes was monitored at 473 K on a prereduced sample, with the sequence starting under CO/He. The NO and CO streams were switched alternatively every 10 seconds for a total of nine switches; little CO_2 or N_2O were formed during this sequence (Figure 1). The initial Rh–Rh coordination number (7.3) was reduced to approximately 4 with the second NO pulse and oscillated between values of 4 and 5 thereafter; these small changes were slower than the pulsing interval. The simultaneous monitoring of the catalysts by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) showed that bridging (1866 cm^{-1}) and terminal (2059 cm^{-1}) CO bands that are typical of sites on metallic rhodium were essentially lost after 10 s of NO exposure; these were replaced by absorptions owing to the $Rh(CO)_2$ unit (2096 and 2031 cm^{-1}) upon exposure to CO. After the second cycle, intensity patterns following the gas switches became established with the two IR bands of the geminal dicarbonyl being formed during CO exposure, and being rapidly lost after switching to NO. A new IR band at 1931 cm^{-1} then emerged, which can be assigned to a linear rhodium nitrosyl on an oxidized rhodium of some form.[8,9]

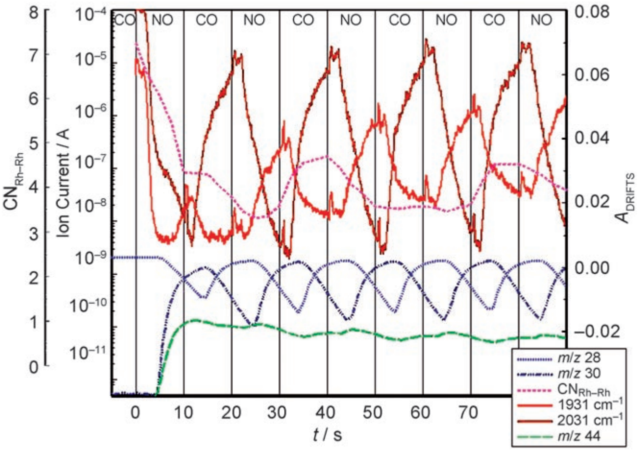

Figure 1. Variations in the detected ion current of *m/z* 28, *m/z* 30, and *m/z* 44 species, the Rh–Rh coordination number ($CN_{Rh\text{-}Rh}$), and the intensity of the $\nu(CO)_{as}$ band at 2031 cm^{-1} and the $\nu(NO)$ band at 1931 cm^{-1} during NO–CO switching over 5 wt% Rh/Al_2O_3 at 473 K. The gas switching times are indicated with vertical lines. Time delays of approximately 2 s and approximately 4 s are apparent to the DRIFTS/XAFS cell and mass spectrometer, respectively.

In the previous temperature-ramp study,[5] significant NO conversion was evident at 573 K, the $Rh(CO)_2$ unit was not observed, and the steady-state Rh–Rh nuclearity had begun to increase. In the isothermal gas-cycling experiment at 573 K, the reduction in the Rh–Rh coordination number was even greater than at 473 K, falling to approximately 2.8 after the second NO pulse and then tracking the switching sequence oscillating between approximately 2.8 (on NO exposure) and approximately 6 (during a CO pulse). At 623 K (Figure 2), the oscillations in the Rh–Rh coordination number varied between about 5.5 after the oxidizing phase of the cycle and increasing to around 8 upon CO exposure. On initial exposure to CO, two $\nu(CO)$ bands were observed owing to atop and bridging sites on metal particles. Switching in NO caused loss of these bands within 20 s, replacing them with the linear nitrosyl with a similar peak intensity but a narrower line width

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[*] Prof. J. Evans, Dr. B. Jyoti, Dr. M. Tromp
School of Chemistry
University of Southampton
Southampton, SO71 1BJ (UK)
Fax: (+44) 2380-593-307
E-mail: je@soton.ac.uk

Prof. A. J. Dent, Prof. J. Evans
Diamond Light Source
Chilton, Didcot, OX11 0DE (UK)

Dr. M. A. Newton
ESRF
6 rue Jules Horowitz, 38043 Grenoble CEDEX (France)

Dr. S. G. Fiddy
CCLRC Daresbury Laboratory
Warrington, WA4 4AD (UK)

[**] We wish to thank the EPSRC for funding this research through grant GR/R60744/01 and the ESRF for a Long Term Proposal. We also wish to thank the staff of the ESRF and of ID24 in particular for the provision of the facilities.

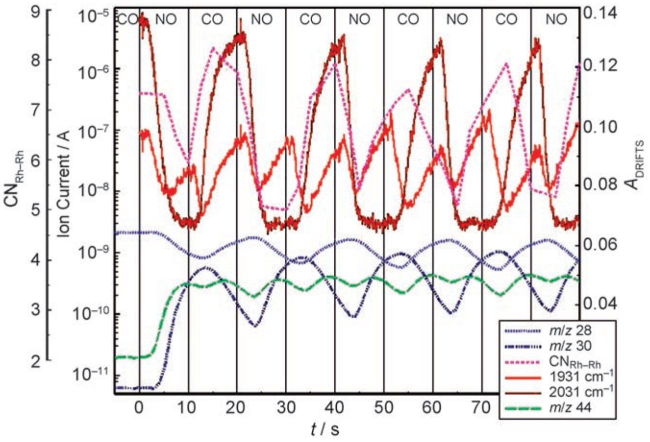

Figure 2. Variations in the detected ion current of m/z 28, m/z 30, and m/z 44 species, the Rh–Rh coordination number, and the intensity of the $\nu(CO)_{as}$ band at 2043 cm^{-1} and $\nu(NO)/(CO)$ at 1907 cm^{-1} during NO–CO switching over 5 wt% Rh/Al_2O_3 at 623 K.

than that of the bridging carbonyl site. Re-exposure to CO at this temperature regenerated the atop and bridging $\nu(CO)$ bands, and after two cycles there was also a cyclical transformation, which is now operating between the oxidized Rh–NO and the CO on rhodium particles. In this temperature range, it is this linear nitrosyl that is observed upon adsorption of NO on Rh/Al_2O_3 and can be implicated in the formation of N_2O.[8] The behavior at 573 K was similar to that observed at 623 K. Furthermore, there was a buildup of lower frequency bands observed at 1622, 1570, and 1472 cm^{-1} owing to adsorption of NO on Rh particles in bridging or hollow sites[10] and/or formation of nitrates or carbonates on the oxide surface.[11] However, only the band near 1910 cm^{-1} closely corresponds with bands identified upon Rh–NO adsorption.[8]

The following conclusions are pertinent to the operation of catalysts like the automotive exhaust catalyst. At 473 K, exposure of CO-covered rhodium, with a mean particle size of about 40 atoms,[12] is substantially fragmented within 10 seconds after exposure to a partial NO pressure of approximately 50 mbar. The residual mean coordination number is probably owing to a small fraction of larger particles. The rhodium can be maintained in this low mean nuclearity both as a nitrosyl or as the geminal dicarbonyl, depending upon the gas composition. At 573 K, the *gem*-$Rh(CO)_2$ is no longer stable, and in the reduction phase of the cycle the rhodium aggregates from an extremely high dispersion (a mean nuclearity of 3–4) back into mean particle sizes of around 20 atoms after exposure for 10 s to CO. At 623 K, the balance moves further towards the persistence of some metal particles, with a mean nuclearity of 60–70 atoms after CO pulsing, which then drops to approximately 13 atoms upon exposure to NO; many of these released rhodium atoms are sequestered as the linear nitrosyl.

Exposure of 5 wt% Rh/Al_2O_3 to 5% NO/He at 573 K results in the dominant $\nu(NO)$ band being near 1910 cm^{-1}. This is a relatively high nitrosyl stretching frequency for rhodium sites when compared with those for $[Rh(NO)Cl_2]_x$ (1770 and 1670 cm^{-1})[13] and $[Rh(NCMe)_4(NO)]^{2+}$ (1758 cm^{-1}),[14] some of which may contain bent nitrosyls. The linear nitrosyl species $[Rh(NO)]^+$, formed by laser ablation of Rh into cryogenic NO/Ne, does exhibit a higher observed frequency in a frozen gas matrix (1958 cm^{-1}).[15] This suggests that the Rh–NO site formed on γ-alumina is indeed electropositive, with little amelioration by the catalyst surface. Extended X-ray absorption fine structure (EXAFS) analysis clearly showed the presence of a new Rh–O/N shell (2.22(2) atoms at 2.03 Å) in addition to the reduction of Rh–Rh coordination number (mean nuclearity of 3–4). Of the more than 20 structures tested, modeling the rhodium nitrosyl as a tetrahedral site with three O ligands and a linear Rh–N–O unit as the major site and with a minor component of the rhodium as fcc particles[16] indeed provided a close fit to the Rh XANES (XANES = X-ray absorption near-edge structure spectroscopy; Figure 3). Hence it appears that, like the *gem*-$Rh(CO)_2$ unit,[6] the Rh–NO unit adopts a site on the surface oxide; this is consistent with the fragmentation of Rh nanoparticles by NO observed by STM on a rutile surface.[17]

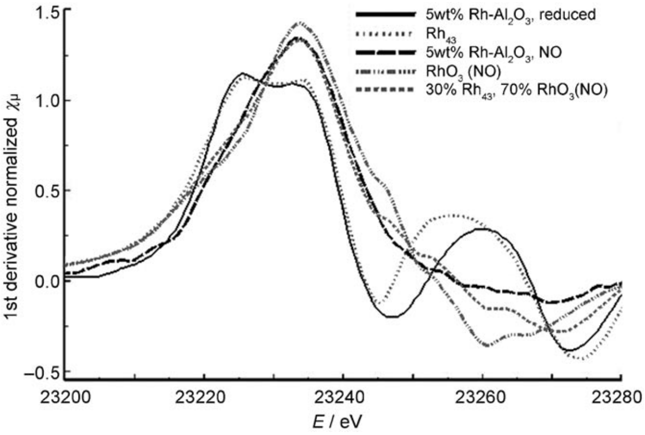

Figure 3. Rh K edge XANES (first derivative of χ_μ in arbitrary units) of 5 wt% Rh/Al_2O_3 before and after exposure to 5% NO/He at 573 K. Simulated spectra of Rh_{43} and a Rh–NO center with three oxygen neighbors are shown.

Comparing the mass spectrometry results at 473 and 573 K (Figure 1 and 2), it is evident that there is a net conversion to species with m/z 28 (N_2) and 44 (CO_2/N_2O). Taking this in conjunction with the IR changes, it appears that reaction of adsorbed CO with NO, forming CO_2 and N_2/N_2O, is approximately two times faster than the reverse reduction of the Rh–NO species by CO.

Thus, the rhodium state for a given surface density of metal is highly dependent upon the ambient gas and the temperature. From a cold start, nanoparticulate rhodium may be substantially dispersed to mononuclear sites under these reactive gases. As the temperature of the catalyst bed is raised, aggregation becomes more favored and the CO/NO redox reaction becomes efficiently catalytic. Even at 623 K, there is evidence of rapid rhodium dispersion into nitrosyl stabilized mononuclear sites and reclustering under reducing conditions. So shifting this balance, as in an engine management system,[18] provides a mechanism of control of particle size if the response times are known. Such declustering may also provide a mode of rhodium release from the catalyst bed.

Experimental Section

The samples of 5 wt % Rh were prepared as described previously from $RhCl_3{\cdot}3H_2O$ and γ-Al_2O_3 (Degussa Alumina C).[4,19] Samples were pretreated in situ with a reduction–oxidation–reduction cycle.

The energy-dispersive EXAFS measurements were carried out on Beamline ID24 at the ESRF operating in 16 bunch mode with a Si[311] Bragg polychromator. The polychromator used a FreLoN phosphor-masked charged-coupled device (CCD) detector,[20] which provides a read-out time of an approximate 1-ms approach when following transformations with a subsecond time resolution.[21] Spectra were recorded with a single frame time of approximately 2.5 ms and averaged over 50 ms for the pulsing experiments. Rapid-scanning DRIFTS spectra were recorded simultaneously by using a Digilab FTS7000 spectrometer, as described previously.[5] The spectrometer was operated at a repetition rate of 64 ms with 4 cm^{-1} resolution. Mass spectra were measured by using a Pfeiffer Omnistar quadrupole mass spectrometer.

Background subtraction used the program PAXAS,[22] with EXAFS analysis with EXCURV98[23] and XANES modeling by using FEFF8.2.[24]

Received: April 2, 2007
Revised: April 16, 2007

Keywords: heterogeneous catalysis · IR spectroscopy · rhodium · synchrotron radiation

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