Toromanoff, *Tetrahedron* **1985**, *41*, 5045. Spectral and analytical data for all new compounds can be found in the Supporting Information. CCDC-177450 (**7a**) and CCDC-177451 (**11a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[21] Subjection of individual isomers *cis*- and *trans*-**16** to 1.5 equiv $TiCl_4$ at $-78\,^{\circ}C \rightarrow 25\,^{\circ}C$ for 90 min resulted in only slight (ca. 5–10%) isomerization at the α center. Therefore, the lack of stereospecificity in **15a** → **16** cannot be fully explained by rapid equilibration at the α-alkyl moiety of the product.

Rapid Phase Fluxionality as the Determining Factor in Activity and Selectivity of Highly Dispersed, Rh/Al_2O_3 in $deNO_x$ Catalysis**

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John Evans*

Rhodium has for many years been a primary component in the make up of auto-exhaust catalysts because of its ability to catalyze the selective reduction of NO_x to N_2.[1, 2] A historical view of this type of system is of an active, but essentially static, phase comprising particulate metal; it is from this axiom that studies of metal single crystals[2] have been accepted as models of macroscopic catalyst behavior. However, it has been established by IR[3] and XAFS[4] (X-ray absorption fine structure) spectroscopy that small rhodium particles (on alumina) undergo corrosive chemisportion to yield a mononuclear $\{Rh^I(CO)_2\}$ species. In addition, the oxidation of Rh/Al_2O_3 under an atmosphere of air and oxygen has also been demonstrated by XAFS.[5] Recently, using in situ, microreactor-based, energy-dispersive EXAFS (EDE)[6] and mass spectrometry[7] we have used the improved time resolution of these techniques to demonstrate that Rh on alumina is rapidly oxidized by NO.[8] Herein we utilize these procedures to probe the correlation between metal structure and catalytic performance for the reduction of NO by H_2.

Figure 1 shows the total NO conversion and N_2O (mass 44) production as a function of reaction temperature and feedstock composition. The net conversions and selectivity of the

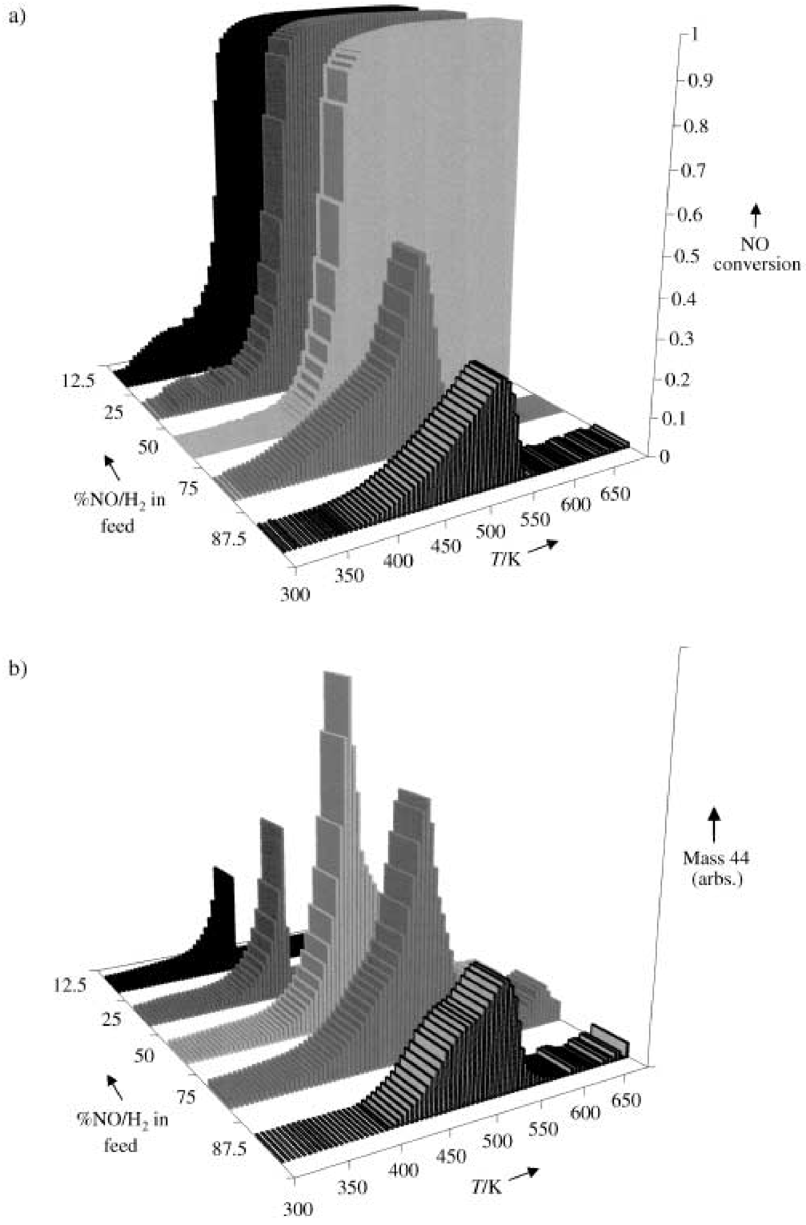

Figure 1. a) NO conversion as a function of reaction temperature and active feedstock composition in the reduction of NO/He by H_2/He over 5 wt% $Rh/\gamma\text{-}Al_2O_3$ catalysts derived from $RhCl_3 \cdot 3H_2O$: catalyst charge: 20 mg; $NO-H_2/He = 4/96$; total gas flow = 10 mL min^{-1}, GHSV ca. $\sim 10^4\,h^{-1}$. b) N_2O production (mass 44) as a function of reaction temperature and active feedstock composition in the reduction of NO by H_2 over 5 wt% $Rh/\gamma\text{-}Al_2O_3$ catalysts derived from $RhCl_3 \cdot 3H_2O$: conditions as for Figure 1a.

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[**] This work was funded under the "Catalysis and Chemical Processes initiative of the EPSRC" and through a "long-term project" allocation of beamtime by the ESRF. We thank the ESPRC (MAN) and ICI (SGF) for postdoctoral funding. The technical skills of John James, Melanie Hill, Sebastian Pasternak, and Ralph Wiegel, are gratefully acknowledged as is the beamline (ID 24) stewardship of Dr. Sakura Pascarelli.

catalyzed process are very sensitive functions of the feedstock composition. The "light off" temperature for the reaction increases as the feedstock with NO proportion until the maximum level of NO conversion drops away markedly as the levels of NO are further increased. Also, as NO levels are increased the catalyst selectivity tends toward the production of N_2O rather than the desired N_2.

Figure 2 shows k^3-weighted Rh K-edge EDE derived in situ during a typical experiment (in this case for the reaction of a feedstock of composition $NO/H_2/He = 1/3/96$), and Table 1 details the results of the analysis in EXCURV98.[9] Reduction in H_2 and purging in He results in an EXAFS signature attributed to particulate Rh. However, under the mixture of $NO/He = 4/96$ at 300 K the EDE is clearly not that of metallic Rh, consistent with a previous report.[5] Even at room temperature, the particulate metal phase has been replaced by a new, oxidic phase (elemental coordintion: $N_1^{Rh} \approx 2.7$). By 420 K the Rh phase has oxidized even further with a distinct reduction in high k EXAFS intensity. This situation changes rapidly thereafter such that at a temperature 15 K higher (435 K) the EXAFS derived from the sample has reverted to a metallic state with N_1^{Rh} of about 8.

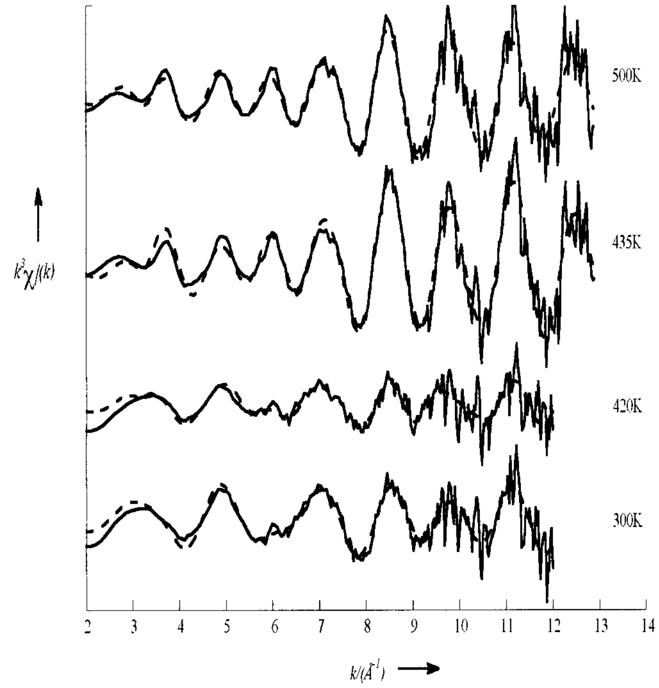

Figure 2. Representative k^3-weighted EDE spectra derived during the reaction of 5 wt% Rh/γ-Al_2O_3 catalysts for a reaction of a feedstock of composition $NO/H_2/He = 1/3/96$ at the temperatures indicated. Each spectrum (solid line) is acquired in 500 ms. The dashed line is the theoretical fit derived from an explicit analysis by using EXCURV 98.

Table 1. Elemental coordination (N_x^s), bond length (R) , and statistical parameters derived from explicit analysis of the EDE spectra shown in Figure 2. Errors in coordination for the oxidic spectra should be regarded as between 15–20%; those pertaining to particulate systems about 10–15%. Errors in bond length determination are estimated at about 2%.

T [K]	Scatterer (s)	N_x^s	R [Å]	$2\sigma^2$ [Å^2]	k_{min}	k_{max}	R [%]
300	O	2.4	2	0.005	2	12	47.6
	Rh	2.7	2.63	0.011			
	Rh	1.9	3.76	0.013			
420	O	2.5	1.99	0.007	2	12	56.6
	Rh	2.4	2.64	0.013			
	Rh	2.2	3.75	0.015			
435	Rh	8.3	2.65	0.014	2	13	36.2
	Rh	3.4	3.74	0.015			
500	Rh	7.9	2.64	0.015	2	13	35.3
	Rh	3	3.73	0.017			

Figure 3 shows in more detail the variation of N_1^{Rh} as a function of reaction temperature and feedstock composition and it is clear that the variations in N_1^{Rh} mirror the total conversion and N_2O production character displayed in Figure 1. The operational phase of the supported Rh catalyst is also therefore a sensitive function of feedstock composition and reaction temperature. As the feedstock is made progressively more oxidizing (increased NO fraction) the formation of particulate Rh is retarded and is not observed at all up to 673 K when the active feedstock mix is $NO/H_2/He = 3.5/0.5/96$. However, even when particulate Rh is observed to be generated the determined value of N_1^{Rh} does not exceed about 8 indicative of nanoparticulate particles containing between 70 and 150 atoms.[10] Furthermore, these processes are observed to be entirely reversible upon the cooling of the system under the feedstock.

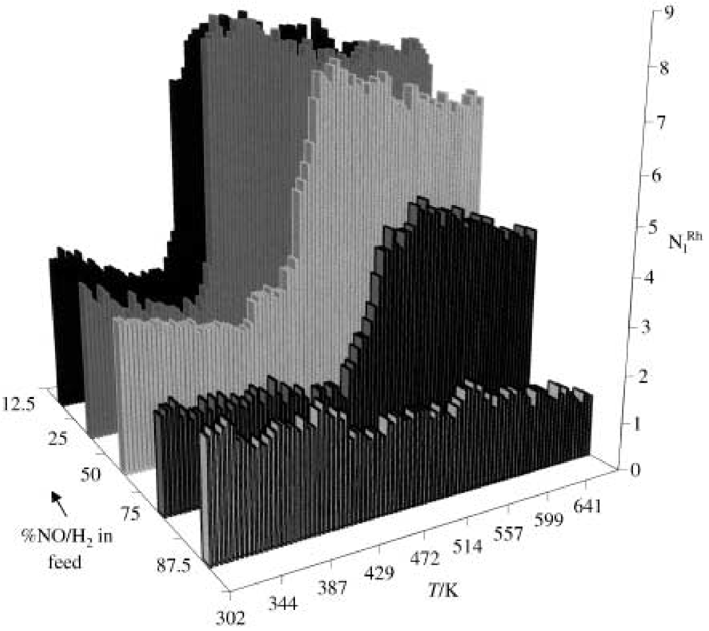

Figure 3. Variation in N_1^{Rh} derived from analysis of alternate EDE spectra collected during NO reduction by H_2 over 5 wt% Rh/γ-Al_2O_3 catalysts as a function of feedstock composition and reaction temperature (conditions as in Figures 1a and b).

More reducing conditions promote Rh particle formation at progressively lower temperatures that tend towards the limit of the intrinsic stability (under H_2) of the oxidic phase that forms spontaneously at low temperature under NO.[8] However, it is the decomposition of this phase that is the precursor of significant NO conversion. It is this phase transition that is also the source of the transient production of N_2O rather than any surface chemistry intrinsic to extended metal surfaces:

below a NO/H_2 ratio of 1, once particulate Rh becomes predominant, a very rapid curtailment of N_2O production is observed. Recent catalytic and infrared work[11] have already suggested that the formation of N_2O requires the presence of both metallic Rh and oxidized Rh sites. This is consistent with our observations for the NO/H_2/He = 2/2/96 gas stream. These results show directly that the presence of rapid phase altering processes can control the behavior of highly dispersed supported metal catalysts rather than the intrinsic surface chemistry of the bulk metal. We have already shown that such processes may occur when nanoparticulate Rh is exposed to both NO[8] and O_2.[12] Interestingly, Rh thin foils and single crystals have been reported to oxidize beyond the surface ad-layer under O_2 above 500 K.[13] A consequence of these phenomena is that the phase of the supported metal at a given gas composition and temperature can be far from static and may result from a dynamic equilibrium between processes that lead to oxidation and those that reductively reform the particulate metal. While oxidation of these Rh/Al_2O_3 catalysts by NO/He = 4/96 is rapid at room temperature, re-reduction of the NO oxidized Rh sites by H_2/He = 4/96 was evident only above 400 K.[8] It is this differential that is directly responsible for the activity and selectivity of the catalyst. These processes may be related to the relatively poor performance of the three-way exhaust catalyst in, for instance, the lean burn conditions,[14] currently favored by the automobile industry on efficiency and environmental grounds; this present study models one component of this.

As can be seen in Figure 1 a, the increase in catalytic activity over a relatively small temperature range is very marked. The rapid oxidative processes may be understood in terms of fundamental, and possibly adiabatic,[15] dissociative chemistry (occurring in the zero coverage limit) on metallic Rh particles.[8] As such we may delineate a set of broad criteria for such a system to develop as follows: 1) dissociative adsorption is facile and highly exothermic, rapidly injecting a large amount of energy into the supported metallic nanocluster; 2) there are poorly effective means for the particle to release this energy through interaction with the gaseous phase or through the particle-support interface; 3) the particles themselves are not large enough to provide an effective energy sink that prevents particle collapse, that is high dispersion; and 4) subsequent reaction with the gaseous environment may result in a new, stable, phase rather than sintering to larger metallic particles.

In summary we have shown that in the limit of high dispersion the nature of oxide-supported metal catalysts may change in oxidizing conditions. Indeed, we have shown that the phases of a supported metal species can be interconverted on time scales that can be deterministic in terms of the activity and selectivity of such catalysts; in this specific case, the selectivity of the reduction of NO by H_2 to N_2 (on reduced, metallic sites) and N_2O (on oxidized sites) can be directly correlated with the phase of the rhodium.

Experimental Section

Aqueous impregnation of $RhCl_3 \cdot 3H_2O$ to γ-Al_2O_3 was used to make 5 wt% Rh catalysts. Samples were dried overnight before being calcined for 6 h at 773 K and then sieved to give a 100 µm fraction. Finally the samples were reduced for 5 h at 573 K under flowing H_2. No attempt to prevent exposure of the sample to air was made prior to it (20 mg) being loaded into quartz tubes (i.d. 3 mm, wall thickness ca. 0.2 mm) and secured in place by using 5 mm long quartz wool plugs. These were then loaded into a microreactor described previously.[6–8] Typical exposure times were 1 ms for I_0 and 3–5 ms for the sample.

EDE measurements were carried out at the ID24 source at the ESRF Grenoble, using an asymmetrically cut Si[111] monochromator in Laue configuration[16] and a masked, Peltier cooled, CCD detector. Energy calibration was referenced with a Rh foil.

Once loaded into a microreactor the samples were purged with He, re-reduced in H_2 at 373 K, and subsequently purged in He again. This procedure resulted in the formation of particulate Rh with a first-shell Rh coordination (N_1^{Rh}) of about 6.5. During catalytic reactions these samples were then exposed to varying compositions of 4% NO/He and 4% H_2/He at a constant flow rate of 10 mL min^{-1} (gas hourly space velocity (GHSV) $\approx$ 10000 h^{-1}) whilst being heated at 10 K min^{-1} from room temperature to 673 K. Simultaneously EDE measurements were recorded at a typical rate of 10 spectra min^{-1} with individual spectra being collected with typical acquisition times of about 500 ms. The reactor was interfaced to a Balzers mass spectrometer station multiplexed to measure sample temperature (from a Eurotherm temperature controller) and 16–20 masses simultaneously. Data reduction and analysis was carried out by using PAXAS[17] and EXCURV98.[9] N_2O and CO_2 were differentiated through their fragmentation and M^{2+} patterns.

Received: December 27, 2001
Revised: April 24, 2002 [Z18437]

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