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The interaction of synthesis gas (CO–H₂) with small rhodium particles

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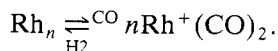
Abstract. The structure of small rhodium particles in a 1% Rh–Al₂O₃ catalyst has been studied *in situ* by EXAFS spectroscopy. After reduction in hydrogen the average particle diameter is $\approx 8 \text{ \AA}$ and the Rh–Rh interatomic distance is $\approx 0.03 \text{ \AA}$ shorter than in the bulk metal ($R = 2.69 \text{ \AA}$). After exposure to carbon monoxide at 1 bar marked changes are seen, similar to those reported by other authors. On subsequent exposure to synthesis gas (a 2 : 1 H₂–CO mixture) at 1 bar and 373 K the catalyst structure reverts to that of the metal, although the Rh–Rh distance has increased to 2.74 \AA . The significance of this result for catalysis by rhodium is discussed.

1. Introduction

Synthesis gas is a mixture of carbon monoxide, carbon dioxide and hydrogen and is an important chemical feedstock. The interaction of the components of synthesis gas with transition metal surfaces has formed part of the basic fabric of surface science investigation for many years. Rhodium is an important metal in heterogeneous catalysis. Its present interest to us is for the single-step conversion of synthesis gas to ethanol:



This is not a commercially viable process, but it is clear that rhodium is the best single-metal catalyst proposed to date [1]. Particular interest in the reactivity of rhodium derives from EXAFS studies published by Koningsberger, Prins and others (KP) [2], where it was suggested that the form of small rhodium particles changed substantially depending on the gaseous atmosphere present. In hydrogen the particles were metallic in structure, but there was considerable disruption in the presence of carbon monoxide. The changes can be represented as an equilibrium:



We have set out to extend the work of KP, and in this progress report we concentrate

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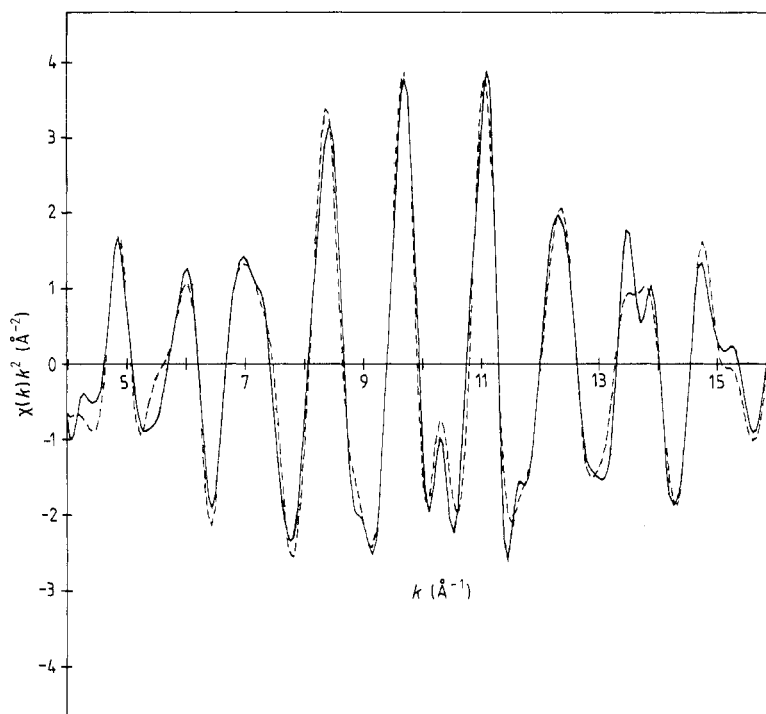


Figure 1. Experimental and theoretical K shell EXAFS spectrum of rhodium foil; parameters used are given in table 1. Full curve, experimental; broken curve, theory.

on the structure of the rhodium particle when CO and H₂ coexist in the gas phase, as will be the case under catalytic reaction.

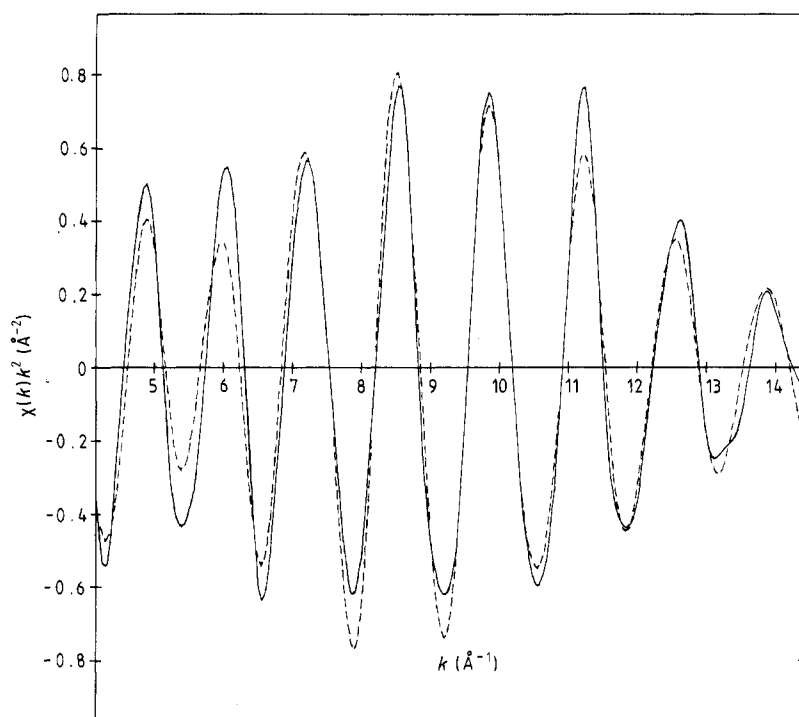
2. Experimental

Catalysts with 1% rhodium by weight were prepared on a γ -Al₂O₃ support using similar methods to those of KP [2]. Supports pre-calcined at 673, 873 and 1073 K were studied in an attempt to vary the surface hydroxyl concentration, but only the 873 K catalyst will be discussed here. X-ray absorption experiments were carried out in an *in situ* cell which has been described previously [3] and which can be operated at pressure up to 1 bar. Samples were studied as pressed discs 3 × 13 mm dia × ≈1 mm thick. Gases were obtained from cylinders (BOC Ltd) and used without further purification. EXAFS measurements were carried out on the Wiggler station at the SERC Daresbury Synchrotron Radiation Source, which was operating at 2 GeV energy and with beam currents in the range 200–300 mA. Data were analysed using standard methods, and theoretical spectra calculated with the single scattering curved wave theory, using the program EXCURVE [4].

Table 1. EXAFS results from rhodium foil and the reduced 1% Rh-Al₂O₃ catalyst.

Rhodium foil						Reduced catalyst		
R (Å)†		Coordination number		Debye-Waller factor (Å ²)		R (Å)†	Coordination number	Debye-Waller factor (Å ²)
EXAFS	XRD	EXAFS	XRD	EXAFS	XRD			
2.689	2.689	12	12	0.008	—	2.65	4.8	0.013
3.78	3.80	6	6	0.010	—	3.73	0.6	0.014
4.67	4.66	24	24	0.011	—	4.59	1.9	0.015
5.28	5.38	18	12	0.011	—	—	—	—
—	6.01	—	12	—	—	—	—	—
7.19	7.11	24	24	0.014	—	—	—	—

† Interatomic distance.

**Figure 2.** Rhodium K shell spectrum for 1% Rh-Al₂O₃ after reduction in hydrogen; parameters deduced are given in table 1. Full curve, experimental; broken curve, theory.

3. Results and discussion

The period of EXAFS oscillations is given by a term of the form

$$\sin(2k \cdot R + 2\delta + \psi_j)$$

where k is the photo-electron wave vector, R is the interatomic distance of interest and

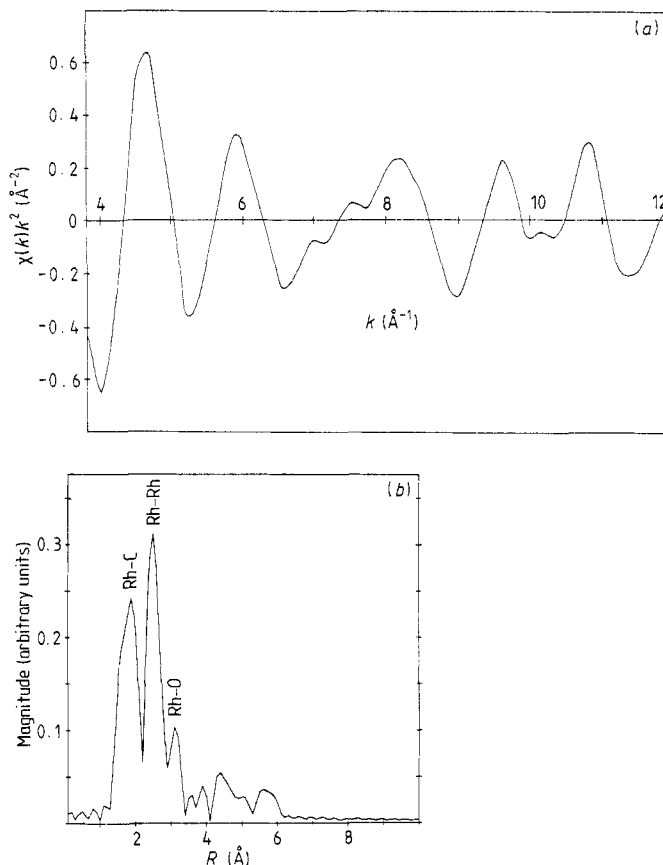


Figure 3. Rhodium K shell spectrum for 1% Rh- Al_2O_3 after reduction and exposure to CO. (a) k space; (b) real-space Fourier transform of (a).

δ and j are phase shift terms. Our practice is to use phase shifts calculated *ab initio*, but modified so that they give good agreement with model compounds of known structure. Figure 1 shows a theory–experiment comparison of the K shell of a rhodium foil sample. The parameters used in the calculation are listed in table 1 and compared with known values. Excellent agreement is obtained, with the only significant deviation in the 2a shell at 5.38 \AA . This is a manifestation of the so-called ‘focusing effect’, where multiple scattering magnifies coordination numbers and distorts interatomic distances for shells where there is an atom directly located between emitter and scatterer.

Figure 2 shows the K shell EXAFS spectrum of the rhodium catalyst after reduction in hydrogen (1 bar) at 473 K and cooling to room temperature. It is dominated by the rhodium–rhodium nearest-neighbour distance. The result of a theoretical spectral simulation, using the phase shifts and other parameters applicable to rhodium foil, is also shown, with the relevant parameters listed in table 1. The low Rh–Rh coordination number is indicative of a very small particle size. A regular 13-atom cluster has a nearest-neighbour coordination of 5.5, which is very close to that reported here, and has a diameter of ≈ 8 \AA .

Our results show that the Rh–Rh nearest-neighbour distance in the small particles, at 2.65 \AA , is smaller than that in bulk rhodium (2.69 \AA). This contraction is a common

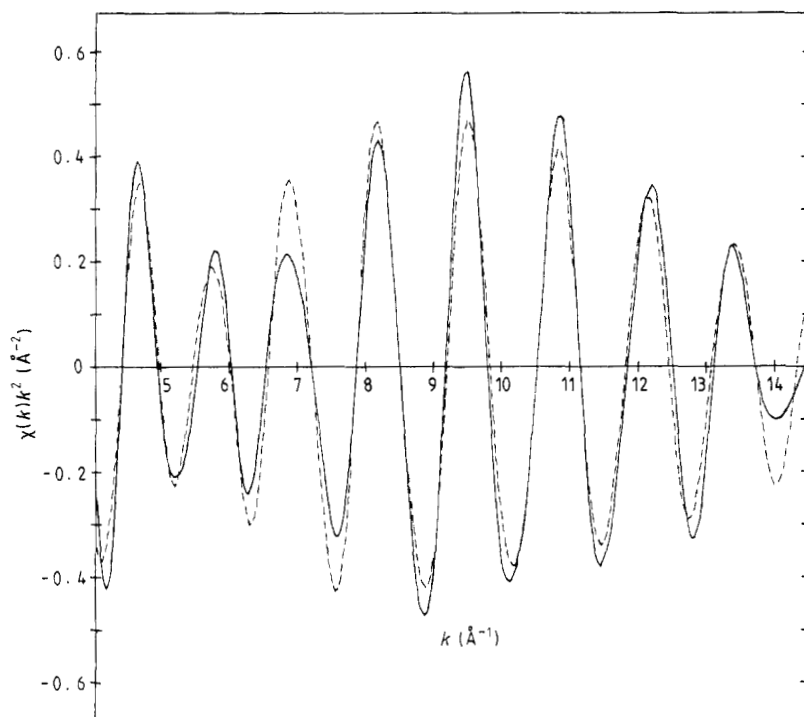


Figure 4. Rhodium K shell spectrum of the catalyst after exposure to synthesis gas at 373 K. Note the similarity of figure 2.

feature of small particles [5] although it was not remarked on by KP. We find no clear evidence for metal–oxygen bonding, which is a controversial claim in KP's study. The analysis is, however, complicated by technical features which will be discussed elsewhere.

The result of exposing the catalysts to CO at 298 K and 1 bar pressure is shown in figure 3(a), (k space) and as the real-space Fourier transform in figure 3(b). The spectrum is markedly changed in comparison to figure 2, and the main features are those already noted by KP, namely a decrease in Rh–Rh coordination number and strong features probably due to Rh–CO bonding.

Figure 4 shows the result of heating the catalyst in synthesis gas ($H_2:CO$ ratio 2:1) at 1 bar and 373 K and a flow rate of 60 ml min^{-1} . The most interesting features of this result are the marked resemblance to figure 2 and the difference with figure 3. The metallic form has been restored to the small rhodium particles and the Rh–Rh distance dominates the Fourier transform. Detailed analysis of this spectrum will be discussed elsewhere, but we note that the Rh–Rh nearest-neighbour distance is now increased compared to rhodium metal, at $\approx 2.74 \text{ \AA}$. The reason for an increase is unclear, but it may reflect σ -donation to the small particle from adsorbed CO.

This result has considerable catalytic significance. Most importantly, it suggests that rhodium exists in the metallic form during synthesis gas reactions, rather than as Rh^+ , as is often assumed as a result of the KP experiments and infra-red spectroscopy studies. Secondly, it is surprising that the equilibrium between the two forms is so readily reversible. KP argue that the driving force for formation of $Rh(1)(CO)_2$ is the greater

strength of the Rh–CO bond compared to the Rh–Rh bond. One would not expect this to be easily reversed by hydrogen, since metal–hydrogen bonds are usually weaker than metal–CO bonds. Yates *et al* [6] have argued that formation of Rh⁺ involves diffusion of rhodium atoms to surface hydroxyl groups, which again one might not expect to be easily reversed.

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