

# Electron optical characterization of a supported rhodium catalyst

A. Legrouri\*

Laboratoire de Chimie Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad, B.P. S15, Marrakech (Morocco)

T. Baird and J. R. Fryer

Electron Microscope Centre, Chemistry Building, University of Glasgow, Glasgow G12 8QQ (UK)

## Abstract

Both fresh and reduced  $V_2O_5$ -supported rhodium catalyst prepared by wet impregnation were characterized by temperature-programmed reduction, CO gas chemisorption (CO-GC), X-ray diffraction and IR spectroscopy. Complementary structural and morphological investigations were carried out using scanning (SEM) and transmission electron microscopies (TEM).

Reduction of the catalyst at 250 °C in hydrogen led to a predominant support reduction to  $V_4O_9$ . Rhodium particles with different shapes and sizes were observed on the surface of this support. The distribution of particle sizes determined from TEM images is compared with that obtained from CO-GC.

## 1. Introduction

Many of the catalysts of scientific and industrial importance consist of small particles supported on carriers. Considerable interest has been directed during the last few years to the use of reducible oxides as carriers [1]. These are known to exert a major influence on metal behaviour by strong interaction [2, 3].

An interest in the mechanisms of metal-support interactions motivated the study of rhodium supported on  $V_2O_5$ . The behaviour of a 1 wt.% Rh/ $V_2O_5$  catalyst was compared with that of a 1 wt.% Rh/ $Al_2O_3$  catalyst for the hydrogenolysis of butane, a reaction for which rhodium is known to be one of the most active catalysts [4]. In the present paper, we report the physicochemical characterization of the Rh/ $V_2O_5$  catalyst. This catalyst, both fresh and reduced, was investigated by temperature-programmed reduction (TPR), CO gas chemisorption (CO-GC), X-ray diffraction (XRD), scanning (SEM) and, predominantly transmission electron microscopies (TEM).

One of the most remarkable attributes of TEM is its versatility. It allows new or established phases to be identified by diffraction or from high resolution images. In addition, it is the most appropriate of physical methods to determine the dispersion of metal particles in metal-supported catalysts [5, 6]. Several reviews have been devoted to the use of TEM for characterization of supported metal catalysts [7–10].

## 2. Experimental details

The 1% in weight rhodium on  $V_2O_5$  catalyst was prepared by impregnating the support, which was prepared from high purity  $NH_4VO_3$  (Aldrich) [11], with an aqueous solution of  $RhCl_3 \cdot xH_2O$  (Johnson Matthey). Following the TPR results, a reduced sample of the catalyst was prepared by heating under a stream of  $H_2$  (50 ml  $min^{-1}$ ) for 2 h at 250 °C.

In our TPR apparatus a mixture of 6% $H_2$ –94% $N_2$  gas (20 ml  $min^{-1}$ ) was directed through the catalyst which was heated at a rate of 5 °C  $min^{-1}$ .  $H_2$  consumption was monitored continuously by a thermal conductivity detector.

CO-GC experiments were carried out at room temperature in a pulse flow system using a 10%CO–90%He gas mixture. The catalyst was activated *in situ* by reduction in flowing  $H_2$  at 250 °C for 2 h.

XRD measurements were carried out with a Philips diffractometer, using  $Cu K\alpha$  radiation ( $\lambda = 0.015418$  nm) at 40 kV and 20 nA.

The IR absorption spectra were registered on a Perkin-Elmer 580-B spectrophotometer from discs containing 2 mg of sample and 300 mg of KBr.

Suitably thin samples for examination by TEM were prepared ultrasonically from suspensions in ethanol. Specimens were mounted on standard 3 mm copper grids covered with a carbon film. Observations were made with a JEOL 1200EX electron microscope.

SEM was undertaken with a Philips 501B instrument operated at 15 kV. Samples were mounted on aluminium stubs and precoated with gold.

\*Author to whom correspondence should be addressed.

### 3. Results and discussion

#### 3.1. Temperature-programmed reduction

The TPR trace of the catalyst (Fig. 1(a)) showed a single peak with its maximum at 155 °C. The uptake of hydrogen measured was far more than was necessary for the reduction of rhodium. This peak can therefore be attributed to the reduction of both rhodium and  $V_2O_5$ . As expected, this peak was absent from the TPR trace of pure  $V_2O_5$  (Fig. 1(b)). The reduction of rhodium, supported on non-reducible oxides such as alumina and silica, was found to occur at 167 °C and 178 °C respectively [12].

#### 3.2. X-ray diffraction

The XRD pattern of the fresh catalyst (Fig. 2(a)) was in good agreement with that found for pure  $V_2O_5$  [13, 14]. The reduced sample exhibited an XRD pattern (Fig. 2(b)) with peaks corresponding to both  $V_2O_5$  and  $V_4O_9$  [15]. It can be seen from the relative intensities that the support was predominantly reduced to  $V_4O_9$ .

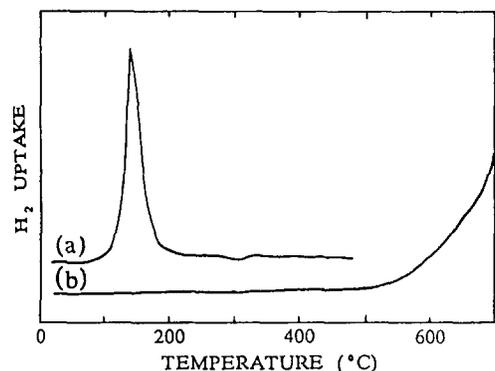


Fig. 1. TPR traces for (a) the fresh catalyst and (b) pure  $V_2O_5$ .

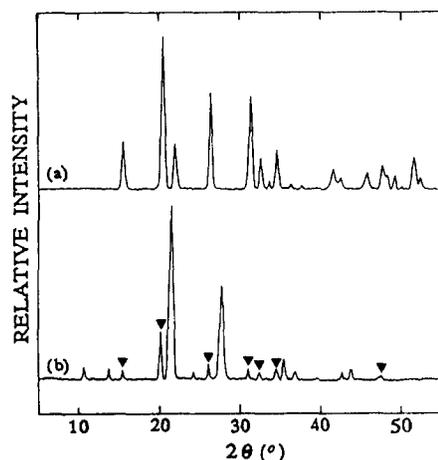


Fig. 2. XRD patterns corresponding to (a)  $V_2O_5$  for the fresh catalyst and (b) a mixture of  $V_2O_5$  (▼) and  $V_4O_9$  for the reduced catalyst.

This reduction was catalysed by the presence of rhodium, as no reduction occurred within detectable limits when pure  $V_2O_5$  was treated under the same conditions.

#### 3.3. IR spectroscopy

The fresh catalyst exhibited an IR spectrum (Fig. 3) which was similar to that found for pure  $V_2O_5$  [14]. Typical of this compound are the bands at 1020 and 995  $cm^{-1}$  which were attributed to the stretching vibration of unshared V=O bonds [16, 17].

The IR spectrum of the reduced sample (Fig. 3) corresponded with that of  $V_4O_9$  [18]. The greater number of peaks in this spectrum, compared with that of  $V_2O_5$ , can be attributed to the fact that vanadium and oxygen atoms occupy more different crystallographic sites in  $V_4O_9$  than in  $V_2O_5$  [19]. In addition, the spectrum represents a  $V_4O_9$  compound with which a certain amount of  $V_2O_5$  is mixed. The considerable weakening of the high frequency bands (1020 and 995  $cm^{-1}$ ) after reduction can be explained by the fact that oxygen atoms of the vanadyl groups, which are known to be the most reactive [20], are more affected by the reduction process.

#### 3.4. Transmission electron microscopy

The crystals which were investigated showed lattice images and electron diffraction patterns (EDPs) of corresponding phases characterized by XRD and IR.

The EDP obtained from the fresh catalyst crystals showed rings and/or spots which could be indexed in agreement with the orthorhombic structure of  $V_2O_5$ . High resolution electron microscopy examination of these crystals showed that the support exposed predominantly the (001) plane, with lattice fringes shown in Fig. 4 corresponding to (200) and (110) planes in  $V_2O_5$

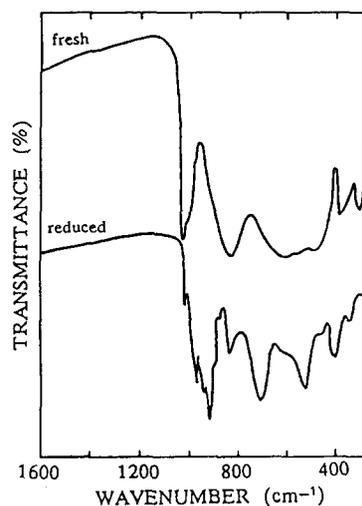


Fig. 3. IR spectra of the fresh and reduced catalysts.

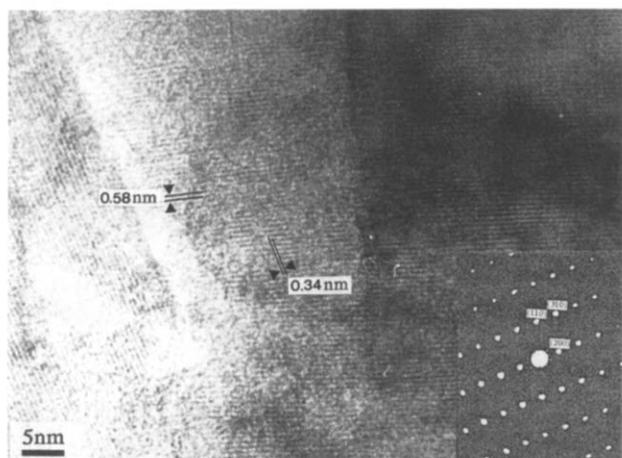


Fig. 4. High resolution electron micrograph of the fresh catalyst with 0.58 nm (200) and 0.34 nm (110) lattice fringes of  $V_2O_5$ . Inset: typical selected area EDP of  $V_2O_5$ .

(a different notation in which the  $b$  and  $c$  axes are permuted is also used for  $V_2O_5$  [21]).

The reduced catalyst gave an EDP with spotty rings which were difficult to index. The complexity of these EDPs might be due to the fact that they contained reflections arising from both polycrystalline  $V_4O_9$  and  $V_2O_5$ . However, structure determination was possible using selected area electron diffraction. The measured angles of  $52^\circ$  and  $38^\circ$  between the (011) and (002) planes and the (011) and (020) planes (Fig. 5) are close to the calculated values of  $51.4^\circ$  and  $38.6^\circ$  for the tetragonal unit cell, described by Theobald *et al.* [15] for  $V_4O_9$ , and are inconsistent with the orthorhombic structure described by Grymonprez *et al.* [22] for the

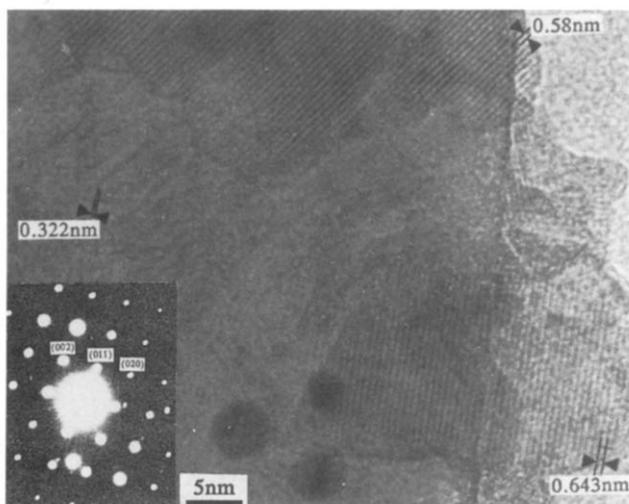


Fig. 5. High resolution electron micrograph of the catalyst reduced at  $250^\circ\text{C}$  showing rhodium particles and single crystals corresponding to  $V_4O_9$  (0.643 nm (011) and 0.322 nm (220)) and  $V_2O_5$  (0.58 nm (200)). Inset: selected area EDP of a  $V_4O_9$  single crystal.

same compound. In addition, lattice fringes corresponding to both  $V_4O_9$  and  $V_2O_5$  were observed by TEM (Fig. 5).

Rhodium particles were also observed on the surface of the support (Fig. 6(a)). The shape of these particles was not easy to define. However, many of them presented a hexagonal shape in projection. Such faceting, via the formation of atomically dense crystallographic planes, is said to be indicative of the most stable situation [23]. The particle size distribution, measured from about 1000 particles (Fig. 6(b)), gave an arithmetic mean diameter of 4.3 nm. This value is a little higher than that determined from CO-GC experiments which was found to be 3.8 nm. This is probably due to non-detection of very small particles by TEM. The visibility of very small particles is known to be affected by strongly scattering supports [8], such as in the present case.

### 3.5. Scanning electron microscopy

Examination of the fresh catalyst by SEM (Fig. 7(a)) revealed that the crystals present the same

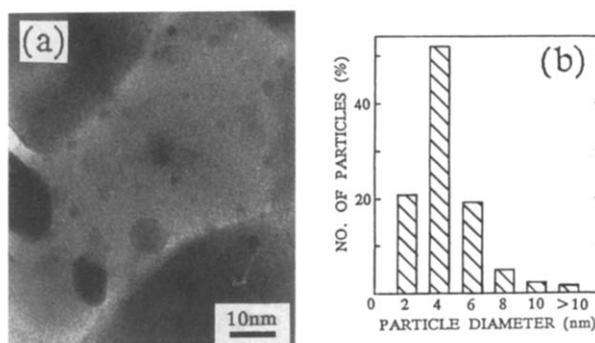


Fig. 6. (a) TEM image of rhodium particles on the reduced catalyst and (b) the corresponding rhodium particle size distribution histogram.

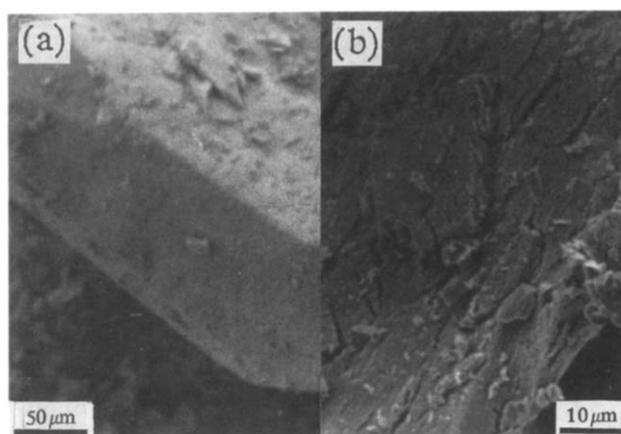


Fig. 7. Scanning electron micrographs of (a) the fresh catalyst and (b) the catalyst reduced at  $250^\circ\text{C}$  showing crack formation.

morphological features as those observed for pure  $V_2O_5$  [14, 24]. Reduction of the catalyst at 250 °C resulted in the formation of cracks at its surface (Fig. 7(b)). The presence of these cracks could be explained by loss of mass due to evolution of oxygen from the bulk of the support during the reduction process and structural rearrangement of atoms to form the lower oxide. Similar morphology observations were made by TEM.

#### 4. Conclusions

A 1%Rh/ $V_2O_5$  catalyst was prepared by impregnation. Consequent to TPR results, it was reduced at 250 °C in hydrogen.

Structural investigation by XRD, IR and TEM showed that the support was reduced largely to  $V_4O_9$  when the catalyst was reduced.

Rhodium particles with different shapes and sizes were observed on the surface of the support for the reduced sample. Their arithmetic mean diameter, determined by TEM, was higher than that obtained from CO-GC, owing probably to problems of detection of very small particles by TEM.

Observations of the morphology of the catalyst by TEM and SEM showed that the support suffered severe shrinkage resulting from mass loss and structural rearrangement of atoms to form lower oxides during the reduction process.

#### Acknowledgment

Thanks are due to Mr M. Zamama (Faculty of Science Marrakech) for useful discussions.

#### References

- 1 K. Foger, in J. R. Anderson and M. Boudart (eds.), *Catalysis—Science and Technology*, Vol. 6, Springer, Berlin, 1984, p. 227.
- 2 B. Imelik, C. Naccache, G. Condurier, H. Praliaud, P. Meriaudeau, P. Gallezot, G. A. Martin and G. C. Vedrine (eds.), *Metal–Support and Metal–Additive Effects in Catalysis*, Elsevier, Amsterdam, 1982.
- 3 G. C. Bond and R. Burch, in G. C. Bond and G. Webb (eds.), *Catalysis (Spec. Period. Rep.)* Vol. 6, Royal Society of Chemistry, London, 1983, p. 27.
- 4 J. H. Sinfelt, *Catal. Rev.*, 3 (1969) 180.
- 5 E. B. Prestridge and D. C. J. Yates, *Nature (London)*, 234 (1971) 345.
- 6 M. Nakamura, M. Yamada and A. Amano, *J. Catal.*, 39 (1975) 125.
- 7 A. Howie, in J. M. Thomas & R. M. Lambert (eds.), *Characterisation of Catalysts*, Wiley, Chichester, 1980, p. 89.
- 8 T. Baird, in G. C. Bond and G. Webb (eds.), *Catalysis (Spec. Period. Rep.)* Vol. 5, Royal Society of Chemistry, London, 1982, p. 172.
- 9 J. V. Sanders, in J. R. Anderson and M. Boudart (eds.), *Catalysis—Science and Technology*, Vol. 7, Springer, Berlin, 1985, p. 51.
- 10 P. C. Flynn, S. E. Wanke and P. S. Turner, *J. Catal.*, 33 (1974) 233.
- 11 A. Legrouri, *Proc. 45th Ann. Meet. of the Electron Microscopy Society of America, Baltimore, MD, 1987*, San Francisco Press, San Francisco, CA, 1987, p. 354.
- 12 B. Boumarafi, *MSc Thesis*, Glasgow University, 1986.
- 13 R. Enjalbert and J. Galy, *Acta Crystallogr. C*, 42 (1986) 1467.
- 14 A. Legrouri, T. Baird and J. R. Fryer, *Reactivity Solids*, 5 (1988) 53.
- 15 F. Theobald, R. Cabala and J. Bernard, *C.R. Acad. Sci. Paris*, C269 (1969) 1209.
- 16 L. Abello, E. Husson, Y. Repelin and G. Lucazeau, *Spectrochim. Acta*, A39 (1983) 641.
- 17 P. Clauws, J. Broeckx and J. Vennik, *Phys. Status Solidi B*, 131 (1985) 459.
- 18 P. Clauws, *Verh. K. Acad. Wet. Lett. Schone Kunsten Belg., Kl. Wet.*, 42 (1980) 159.
- 19 K.-A. Wilhelmi, K. Waltersson and L. Kihlberg, *Acta Chem. Scand.*, 25 (1971) 2675.
- 20 B. K. Tarama, S. Teranishi, S. Yoshida and T. Tamura, *Proc. 3rd Int. Congress on Catalysis, Amsterdam, 1964*, Vol. 1, North-Holland, Amsterdam, 1965, p. 282.
- 21 H. G. Bachmann, F. R. Ahmed and W. H. Barnes, *Z. Krist.*, 115 (1961) 110.
- 22 G. Grymonprez, L. Fiermans and J. Vennik, *Acta Crystallogr. A*, 33 (1977) 834.
- 23 S. Fuentes and F. Figueras, *J. Catal.*, 61 (1980) 443.
- 24 A. Legrouri, T. Baird and J. R. Fryer, in L. M. Brown (ed.), *Electron Microscopy Analysis, Inst. Phys., Conf. Ser.*, 90 (1987) 31.