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HRTEM study of the morphology of RuS_2 supported particles

Mimoun Aouine [a], Christophe Geantet [a,*], Thierry Epicier [b]

[a] Institut de Recherches sur la Catalyse — CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France
[b] Groupe d'Etudes de Métallurgie Physique et de Physique des Matériaux,
UMR CNRS 5510, INSA de Lyon, 69621 Villeurbanne Cedex, France

Abstract

Nanoparticles of ruthenium disulfide supported on silica have been characterized by high resolution transmission electron microscopy. Lattice resolution images were obtained and provided the morphology of the RuS_2 nanoparticles. The interpretation of the atomic resolution images was performed with the help of image simulations, which enabled the atomic columns to be correctly positioned and the thickness of the nanoparticles to be estimated. Several surface planes, such as (2 0 0) or (1 1 1), which are supposed to present different catalytic activities, have been identified. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the field of hydrotreating catalysts, extensive research has been carried out on new active phases in order to replace MoS_2 based catalysts. Among the transition metal sulfides (TMS) studied, RuS_2 rapidly appeared as one of the most promising new active phase. As compared to other unsupported transition metal sulfides, the catalytic activity of RuS_2 in the conversion of model molecules was found to be one of the highest [1,2]. Similar trends have been observed in the supported state, e.g. on carbon [3,4]. Then, specific studies dedicated to RuS_2 supported on various oxides such as alumina [5], silica [6], zeolites [7] have been performed for applied or fundamental purposes. It has been suggested that the most frequently exposed planes are the (1 0 0) and (1 1 1) surfaces [8,9]. In several cases these active phases were found to present outstanding properties particularly in the case of hydrogenation of aromatics. These catalytic properties have been partly explained by the high capability of RuS_2 nanoparticles to heterolytically activate hydrogen [10]. These results stimulated theoretical works: Hartree–Fock ab initio calculations of the geometric and electronic structure of (1 0 0) and (1 1 1) surfaces of RuS_2 revealed high discrepancies between the two surfaces [11]. Then similar calculations were performed on the activation of H_2 and H_2S on (1 0 0) and (1 1 1) surfaces. These studies revealed that the (1 1 1) plane is highly reactive towards these molecules [12], whereas (1 0 0) plane is poorly reactive [13]. The problem of structure sensitivity has rarely been evoked in the catalysis by sulfides but everybody agrees on the fact that in the case of MoS_2 lamellar nanoparticles, the basal plane (0 0 0 1) is inactive, whereas active sites are localized at the edge of the particles on (1,0,−1,0) or (1,1,−2,0) planes. Apparently, even if RuS_2 presents an isotropic structure, the theoretical calculations suggest that structure sensitivity may also occur. At medium magnifications ($200\,\mathrm{K} < G <$

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[*] Corresponding author. Tel.: +33-4-72-44-53-36;
fax: +33-4-72-44-53-99.
E-mail address: geantet@catalyse.univ-lyon1.fr (C. Geantet).

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300 K), TEM images revealed that RuS_2 particles are nearly spherical, and their sizes are comprised between 2 and 10 nm, depending on the nature of the support or the loading deposited [5,6]. High resolution transmission electron microscopy (HRTEM) is a unique tool which can provide nanoscale informations on the shape of individual particles of a catalyst deposited on a high surface area support [14,15]. However, due to tilt conditions, images of lattice fringes are not directly related to structural informations, while atomically resolved images offer a better guarantee to identify the orientation and the structure of small particles [16]. Modern TEMs present point-to-point resolution below 0.2 nm which leads to atomic resolution, but further image treatments (i.e. Fourier transform, image filtering) as well as computer simulations are generally required. In the field of catalytic nanoparticles of transition metal sulfide, HRTEM has only been used for the characterization of unsupported doped or undoped molybdenum disulfide [17]. The purpose of this study was to use HRTEM in order to get a complete description of the morphology of the RuS_2 nanoparticles deposited on silica.

2. Experimental

2.1. Catalysts preparation

The preparation of RuS_2/SiO_2 (7 wt.% of Ru, SiO_2 Grace Davison 432, 300 m^2/g) has been previously described in Ref. [6]. After impregnation, the dried catalysts were heated at 673 K for 2 h under a N_2/H_2S 15% gas mixture to perform sulfidation.

2.2. High resolution transmission electron microscopy, image simulation

High resolution electron microscopy (HREM) was performed with a 200 kV JEOL 2010 microscope, with a point resolution of 0.195 nm (coefficient of spherical aberration $C_s = 0.5$ mm). Further analytical work was performed on the 200 kV field-emission microscope available at the CLYME (Consortium LYonnais de Microscopie Electronique). This instrument (JEOL 2010F) is equipped with an EDS X-ray analyzer LINK-ISIS (spatial resolution ∼1 nm) and an electron energy-loss PEELS spectrometer 666-GATAN (minimum energy spread ∼0.65 eV, effective analysis possible down to a probe size equal to 0.4 nm). Freshly sulfided samples were ground under an inert atmosphere and were ultrasonically dispersed in ethanol. The suspension was collected on carbon-coated grids. HREM image simulations and matching were performed using the multislice approach included in the SIMPLY-SHRLI package [18].

3. Results and discussion

Ruthenium disulfide belongs to the family of transition metal dichalcogenides crystallizing in the pyrite structure (space group Pa3, $a = 0.56095$ nm, with Ru^{2+} in 4(a) and S^{-} in 8(c), with $x = 0.3879$) [19]. Consequently, the supported particles of RuS_2 are expected to exist in the form of tridimensional aggregates. A typical conventional TEM picture of a supported RuS_2 catalyst reveals nearly spherical particles dispersed on the support, with an average size ranging from 2 to 10 nm (see Fig. 1). EDS analysis has been performed on several particles using a probe size of 2.4 nm, and the average results are S: 66.29 at.%, Ru: 33.71 at.%, which corresponds fairly well to RuS_2.

At higher magnification, mono- or two-dimensional lattice fringes are frequently observed in the RuS_2 particles (see Fig. 2).

Fig. 3 shows an isolated RuS_2 particle and the computer treatments that have been performed on an experimental image in order to provide a geometrical modeling of the particle. This image was obtained along [0,−1,1] direction, and {1,1,1} planes are clearly present at the surface of this particle. This zone axis has been obtained on more than 10 other particles observed at atomic resolution (see e.g. Fig. 4) , but two other azimuths have been observed, i.e. [1,0,0] and [−2,4,1] directions.

3.1. Image simulations

HRTEM images contain atomic information at a local range; depending upon the thickness and defocusing conditions, the position of atomic columns can be ascertained with the help of image simulations [20,21]. In the case of RuS_2 supported nanoparticles, we obtained several atomic scale images which have been interpreted and simulated in order to provide a fine

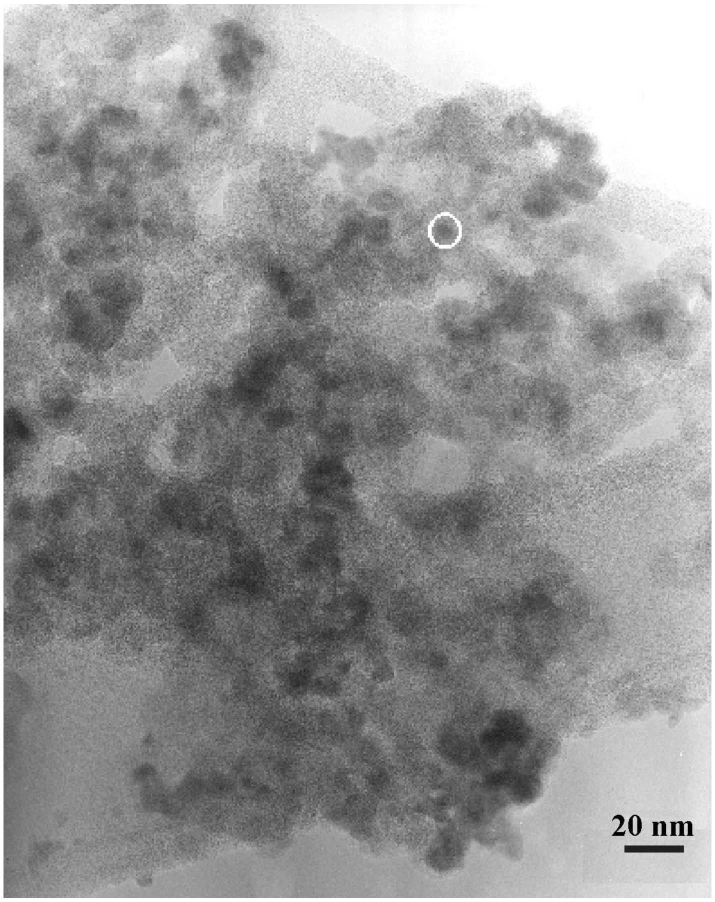

Fig. 1. Conventional TEM picture of RuS_2/SiO_2 catalyst (the white circle points out a RuS_2 particle).

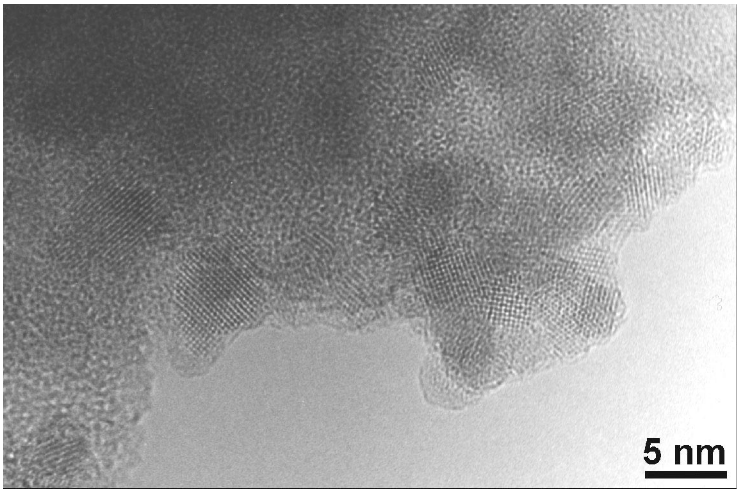

Fig. 2. Lattice fringes images of RuS_2/SiO_2 supported catalysts.

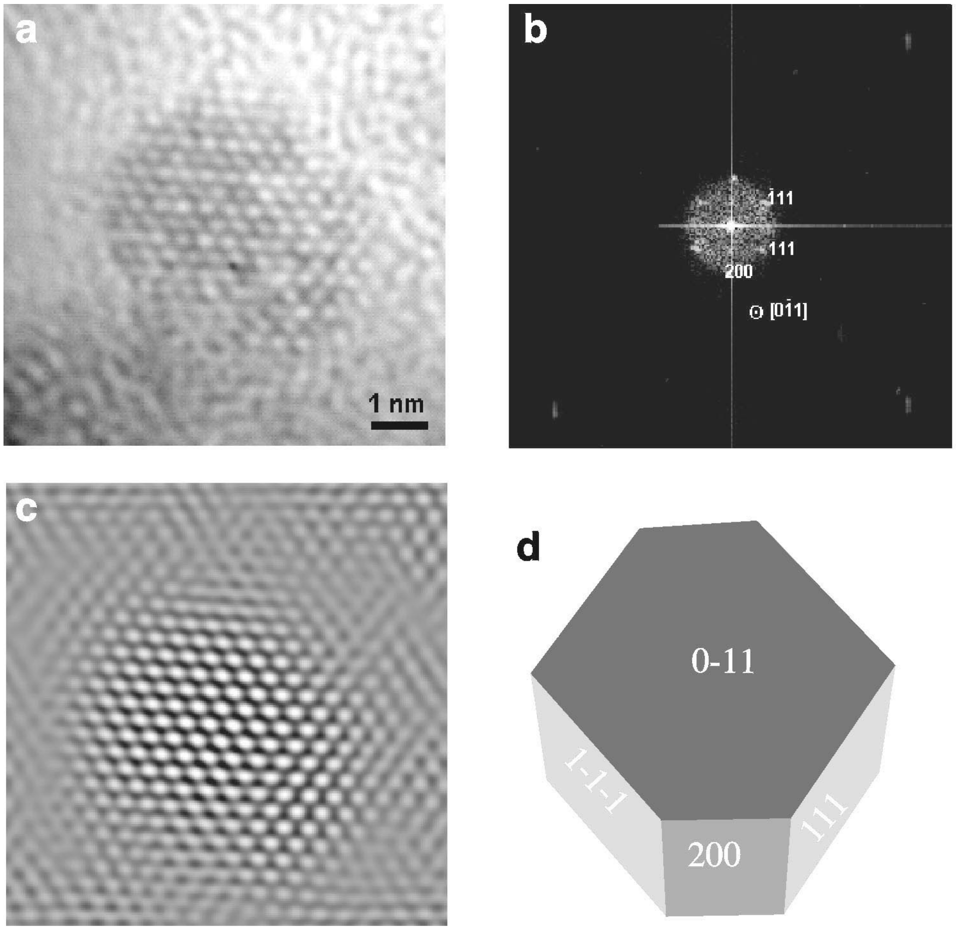

Fig. 3. Geometrical analysis of an isolated RuS_2 particle: (a) experimental image; (b) Fourier transform; (c) filtered image; (d) modeling of the particle.

description of the particles. Rigorously, matches between simulation and experimental images require a series of TEM images obtained with several defocusing conditions. In the case of RuS_2 supported particles, the stability of the particles under the electron beam is weak and it was not possible to take several pictures of the same particle. However, one advantage of small particles supported on a non-crystalline medium regarding the estimation of realistic experimental parameters for the simulations (i.e. the values of thickness and defocus) is that those parameters can easily be determined from the experimental images. The thickness can be evaluated from the direct measurement of the lateral size of the particles, assuming an isotropic shape (which is the case for the present RuS_2 particles; see Figs. 1 and 2); the defocus can be evaluated from numerical diffractograms obtained from the non-crystalline regions of the micrographs. Then, both values can be used as a starting point of a quantitative matching procedure of the experimental image, as permitted in the SIMPLY-SHRLI software [22]. Fig. 4 shows a complete analysis of a particle illuminated under the [1,−1,0] zone axis (see figure caption for details). According to the above statement, the estimated values of thickness and defocus are $t = 4.5 \pm 1$ and $\delta f = -57 \pm 5\,\mathrm{nm}$, respectively; the values refined through the quantitative image matching procedure are $t = 4$ and $\delta f = -55\,\mathrm{nm}$, respectively

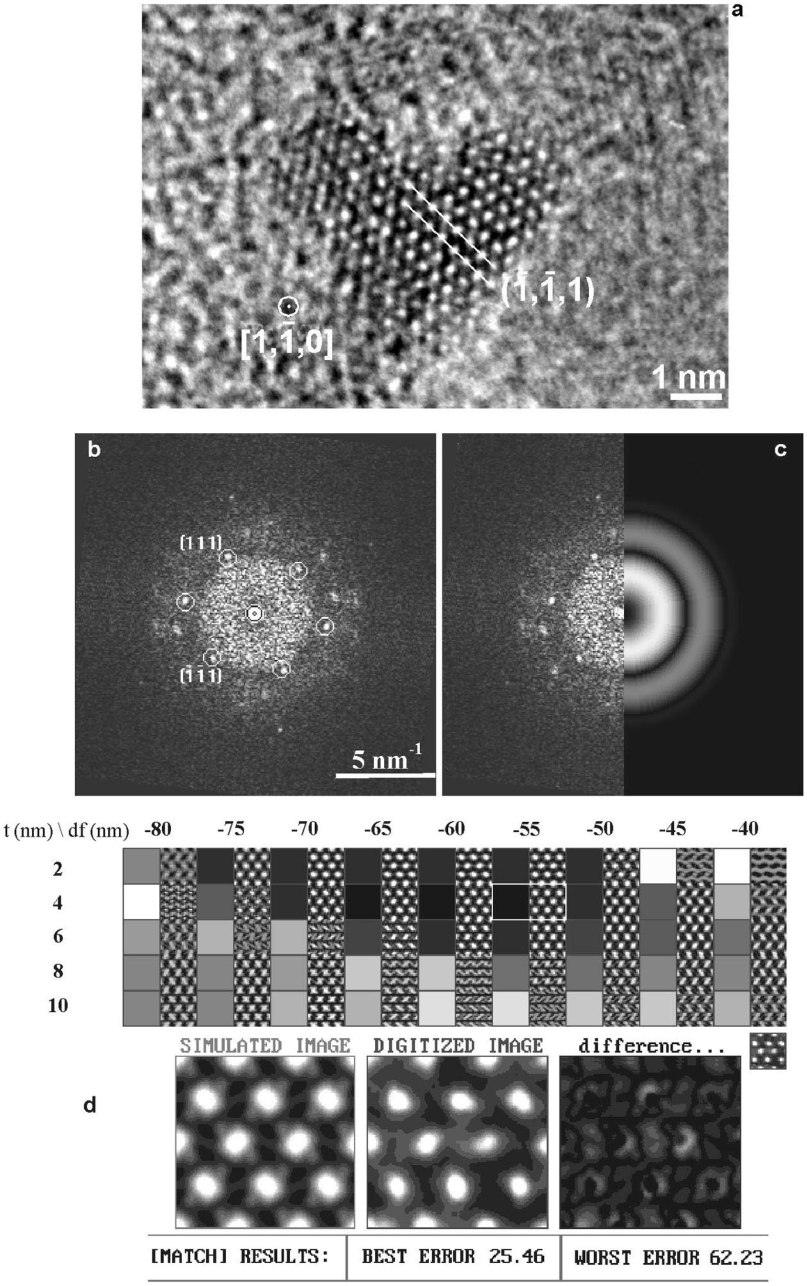

Fig. 4. HRTEM analysis of a RuS$_2$ particle on silica observed in the [1,−1,0] direction: (a) experimental image; (b) numerical diffractogram, showing the indexing of RuS$_2$ reflections (the (1 1 0) and (0 0 1) kinematical extinctions are respected, owing to the small thickness which insures the validity of kinematical diffraction conditions); (c) plot of the expected diffractogram for a defocus equal to -57 nm, plotted with the software Diffraction-Workshop [22]; (d) quantitative image matching procedure: an image agreement factor (IAF) has been calculated between the experimental digitized image (bottom right) and images simulated for a range of thicknesses and defoci as indicated (simulation parameters for the JEOL 2010 microscope: defocus spread $\Delta F = 12.5$ nm, convergence half-angle: 0.9 mrad). For each image, the IAF is displayed graphically (white: maximal 'worst' error, dark: minimal 'best' error, shown by the white frame and further illustrated by the images shown in the bottom line); (e) final enlargement of the experimental digitized image (left) compared to the simulated image (right) producing the best match at $t = 4$ nm and $\delta f = -55$ nm; atomic columns are superimposed (smallest atoms: S, largest atoms: Ru).

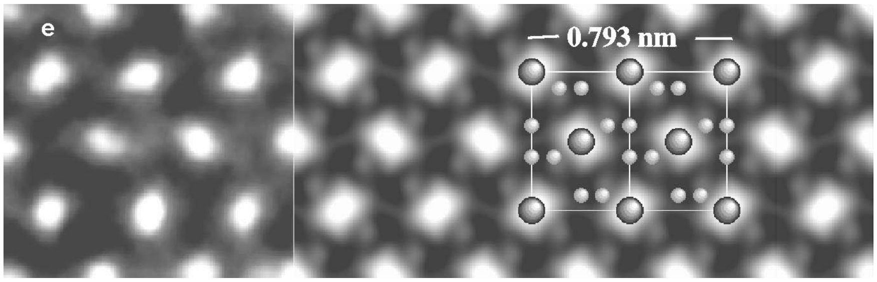

Fig. 4. (*Continued*).

(i.e. close to the optimum 'Scherzer' defocus $\delta f_S = -42.5\,\mathrm{nm}$, equal to $-(C_s\lambda)^{1/2}$, where λ is the electron wavelength equal to 0.0025 nm at 200 kV). These final values are in very good agreement with the starting and experimentally deduced ones. Fig. 4e shows that under such imaging conditions, the heaviest atoms (Ru) appear as white dots on the experimental image; representation of the projection of atoms (superimposed on the right part of Fig. 4e) provides also the location of sulfur pairs. Then, this technique provides a complete description of the nanoparticles in terms of location of the two kinds of atoms.

4. Conclusion

HRTEM imaging of RuS_2 supported particles, together with image simulations, gives detailed information on the morphology of the sulfide nanocrystallites (location of S and Ru atoms, thickness of the particle, surface planes). The types of facets which have been evidenced correspond in a large part to the $\{1,1,1\}$ family. As suggested by theoretical studies, these planes are supposed to be much more active for hydrogen activation than $\{1,0,0\}$ planes.

This work illustrates that atomic resolution can be obtained on sulfide nanoparticles and amorphous supports. It is with Scanning Tunneling Microscopy, one of the few techniques, providing the atomic scale structure of such sulfides nanoclusters [23].

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