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EUROCAT oxide: an European V_2O_5–WO_3/TiO_2 SCR standard catalyst study Characterisation by electron microscopies (SEM, HRTEM, EDX) and by atomic force microscopy

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Abstract

The morphology and the homogeneity in chemical compositions of fresh and used V_2O_5–WO_3/TiO_2 EUROCAT SCR samples, in their original monolith form and after gentle grinding, have been investigated by means of electron microscopies and EDX analyses. It appears clearly that the monoliths were constituted of fibres rich in Si, Al and Ca embedded without preferential orientation in a nearly homogeneous oxide phase containing Ti, V, and W. This phase was in the form of small particles of homogeneous size of around 20–40 nm. The used catalyst was very similar to the fresh one, only the presence of S element and of more defects and more fibres were observed on the surface of the monolith. This observation was confirmed by a higher roughness detected using AFM technique.

EDX–TEM studies on the powders obtained by gently grinding the monoliths have shown that W and V species were well distributed in TiO_2 support and that the repartition of the W species, very homogeneous in the fresh sample, became somewhat slightly more heterogeneous in the used sample. V species were not so well dispersed that W species and even, some particles rich in V were observed on the used sample. This may be due to the migration and agglomeration of some of the V species. More particles, very rich in Si, were also observed for the used sample suggesting that the coating of the fibres by the active phase was partly deteriorated during SCR reaction. This observation was supported by an AFM analysis which showed a higher surface roughness for the used sample.

It was also observed by high resolution TEM that the first one or two atomic layers at the surface of all crystallites appear amorphous, while the further layers are well crystallised with the anatase structure. For the used sample this amorphous layer is slighly larger. This is an important feature for electrical conductivity (mainly at the surface) and catalytic properties.

Keywords: EUROCAT oxide; Electron microscopies; Atomic force microscopy

1. Introduction

Electron microscopies are very useful tools to investigate the morphology and the uniformity of particle shape and size from macroscopic to atomic scales.

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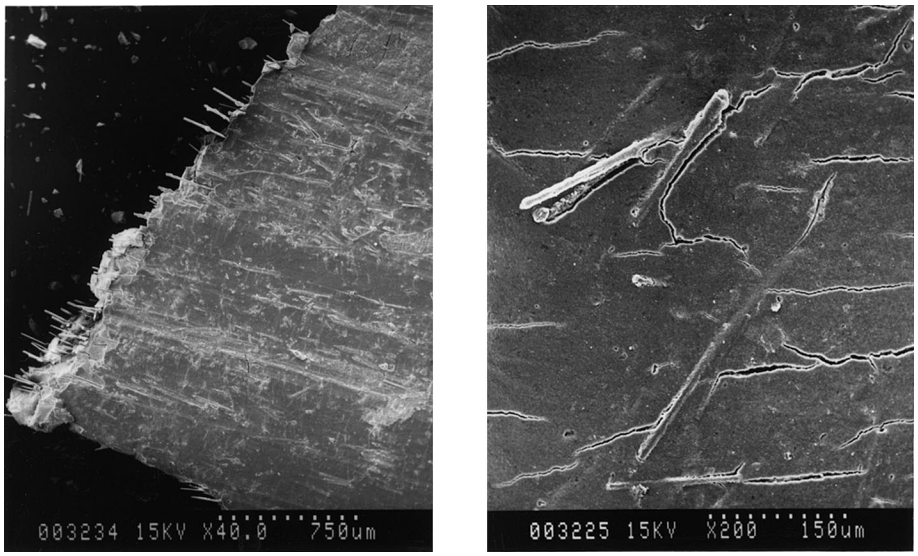


Fig. 1. SEM images at low magnification of the fresh (left) and used (right) monolith samples.

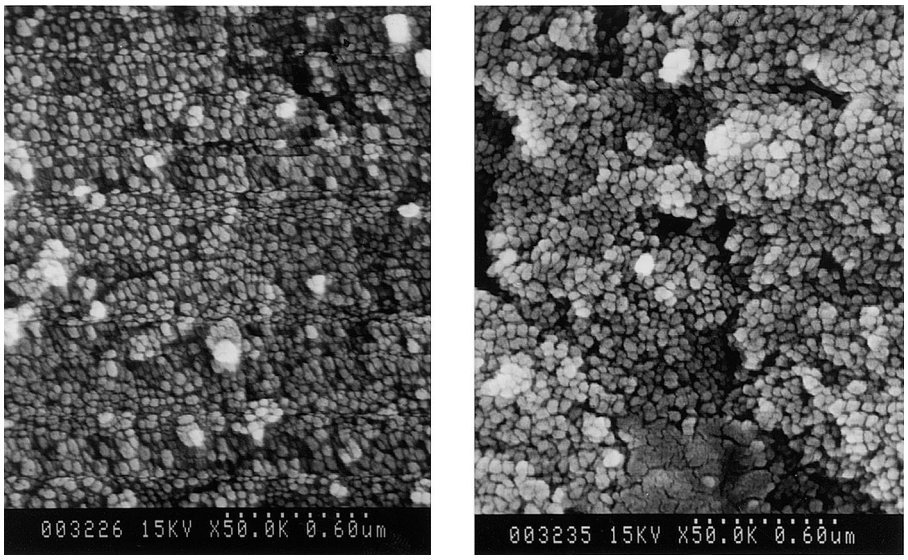


Fig. 2. SEM images at high magnification (5×10^4) of the surfaces of the fresh (left) and used (right) monolith samples.

Scanning electron microscopy (SEM) gives mainly morphological informations with magnification varying from 200 to 50,000. Combined with energy dispersive detection of emitted X-ray photons, it permits to determine the chemical homogeneity of the catalysts at a mesoscopic scale. A distribution of the elements may also be obtained by imaging the back-scattering electrons.

High resolution transmission electron microscopy (HRTEM) with magnification from 2×10^4 to 5×10^5 combined with energy dispersive X-ray absorption (EDX) provides quantitative information on the

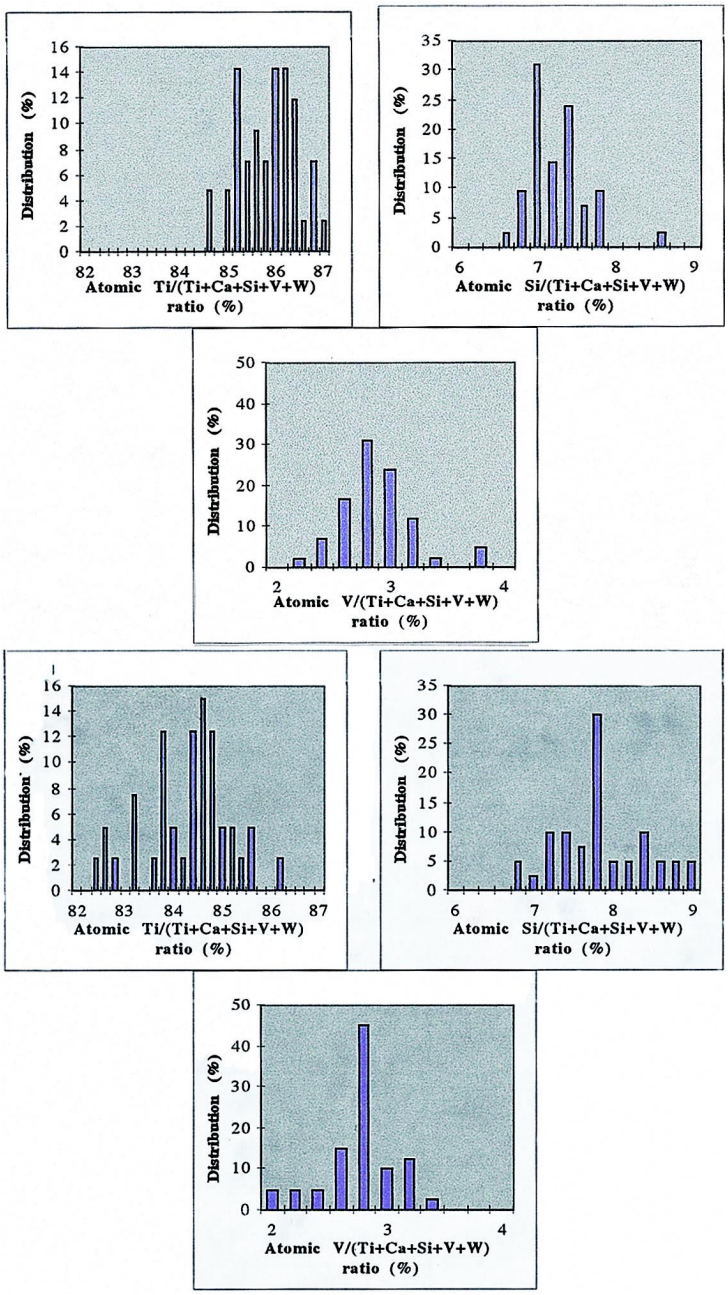


Fig. 3. Distribution of Ti, Si, V elements for the fresh (top) and used (bottom) monoliths (large areas analysed: 0.1–1 cm^2) obtained with CAMECA EDX–SEM.

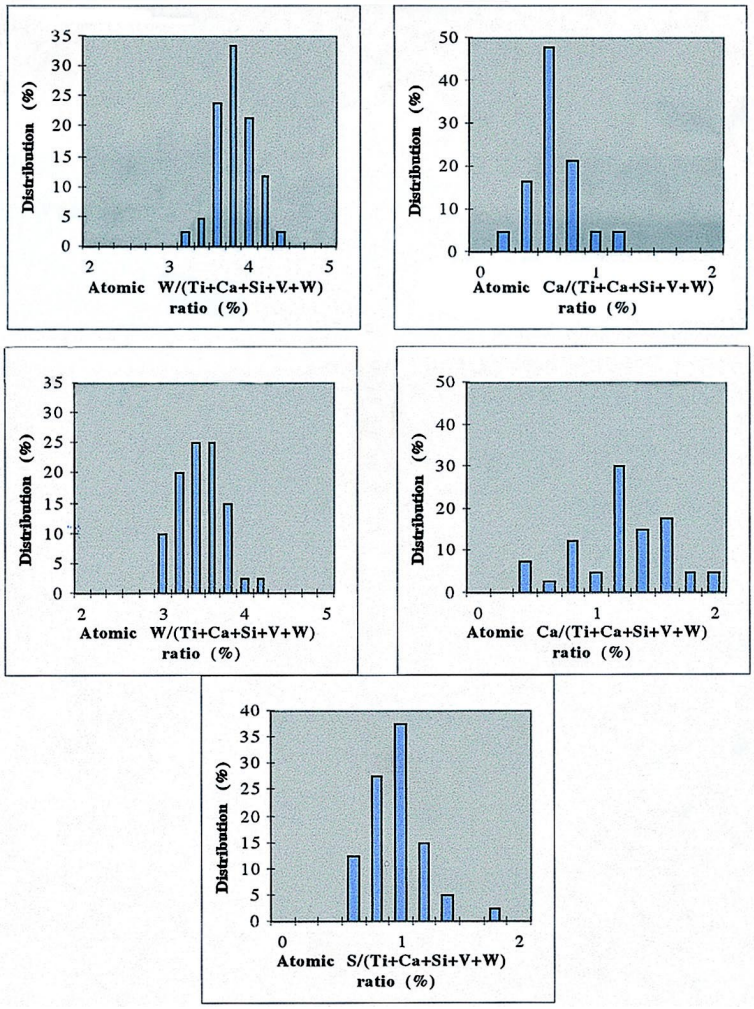


Fig. 4. Distribution of W, Ca and S elements for the fresh (top) and used (bottom) monoliths (large areas analysed: 0.1–1 cm^2) obtained with CAMECA EDX–SEM.

local crystallisation state and chemical composition of ensembles of particles and of isolated particles.

Atomic force microscopy is also capable to give morphological informations under any ambient atmosphere, even at atomic scale.

2. Experimental

2.1. SEM

Some investigations were performed on small flat pieces cut from the fresh or used monoliths and on the powder obtained by gently grinding the monoliths. The samples were pasted on a sample holder using carbon tape and then covered with a gold–palladium film by cathodic pulverisation. Observations were carried out on a Hitachi S800 microscope (CMEABG Centre, University of Lyon 1), with a 15 kV electron beam.

Other investigations were performed on three flat pieces containing two or three channels of monolith from three different positions of the fresh and used catalysts, in order to investigate their uniformity. The samples were covered with a carbon film (thickness around 40 nm) from a carbon tape in vacua. Moving along each channel, some regions were analysed to de-

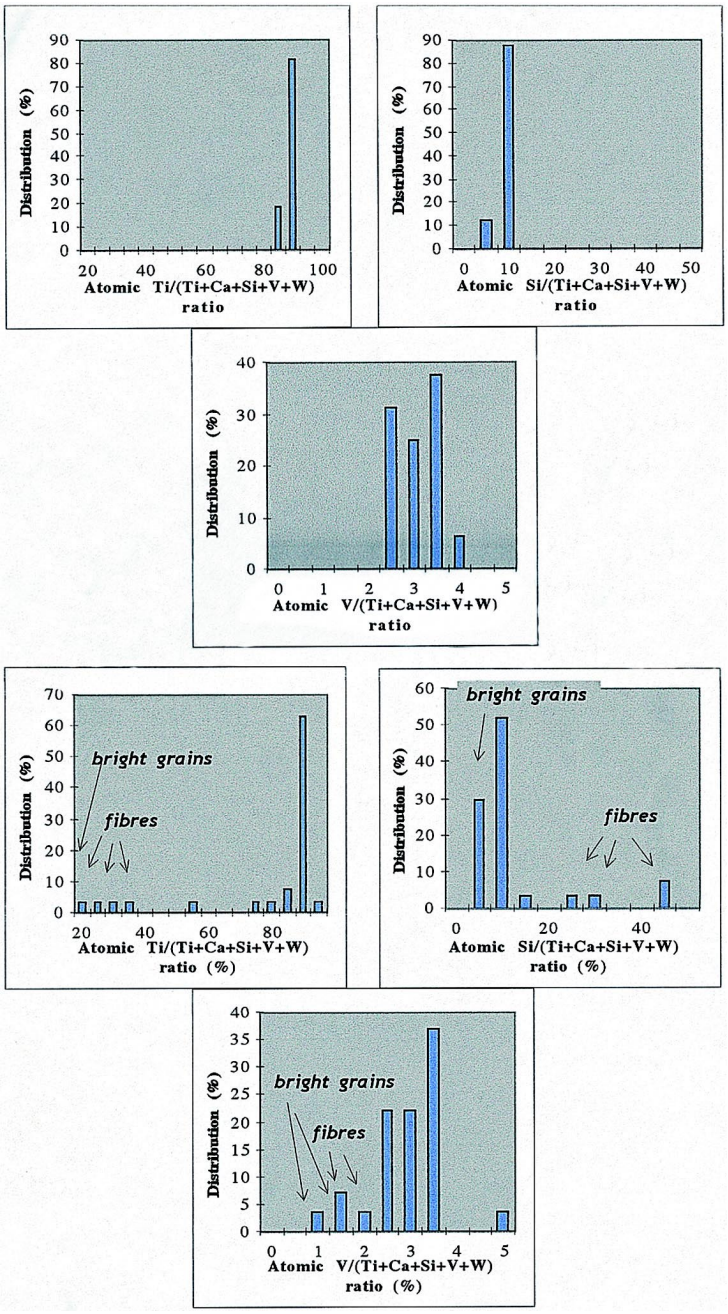


Fig. 5. Distribution of Ti, Si, V elements for the fresh (top) and used (bottom) monoliths (small areas analysed: 0.5 μm×0.5 μm) obtained with CAMECA EDX–SEM.

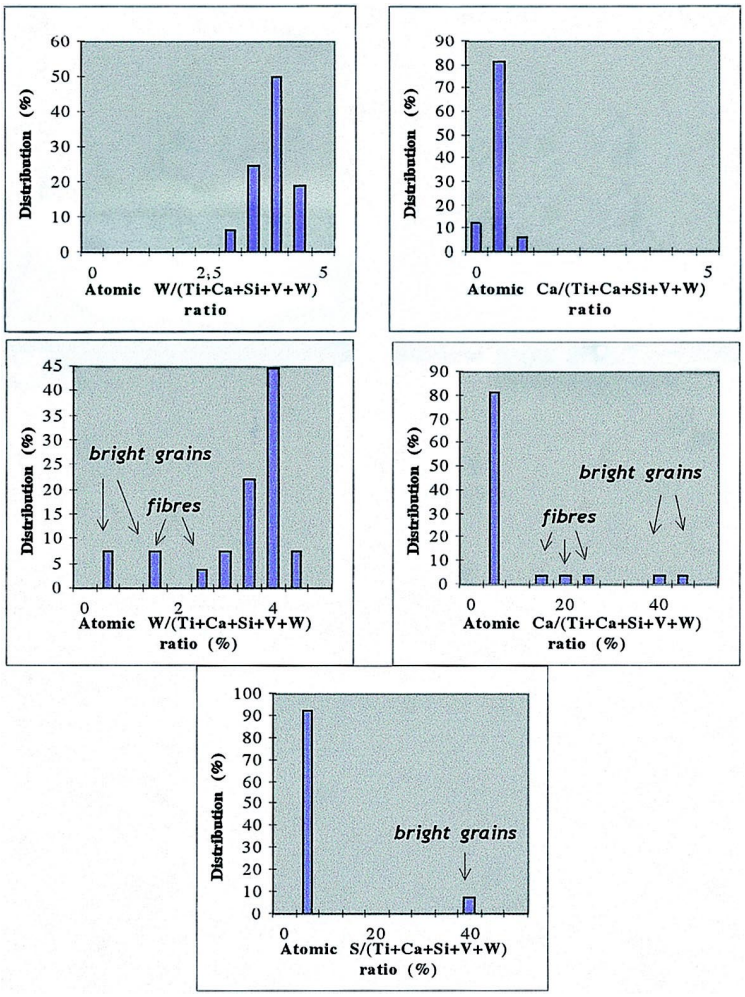


Fig. 6. Distribution of W, Ca and S elements for the fresh (top) and used (bottom) monoliths (small areas analysed: 0.5 μm×0.5 μm) obtained with CAMECA EDX–SEM.

termine the surface composition by EDX, the analysed surface varying between 3.125×10^{-4} and 1.44 cm^2. A fixed probe with a diameter equal to 0.5 μm^2 was also used, the analysis being performed on flat surfaces, bright grains, cracks and fibres. The apparatus was a Camebax microscope. The voltage used was 20 kV in order to detect W. The elements detected by EDX were O, V, W, Ti, Si, Ca, S, using the L radiation for W and the K radiation for the other elements.

A mapping was also done along one channel of the fresh monolith with an analysed area of 0.36 cm^2.

2.2. TEM–EDX

Powdered samples were obtained by gently grinding the monoliths. Then they were dry dispersed on a copper grid and finally covered with a holey carbon film. Observations were performed on a Jeol 2010 microscope with a 200 kV electron gun. The EDX analyses were carried out with a 25 nm probe, on areas varying from 100 to 700 nm^2, on different ensembles of particles and on several particles taken in each ensemble.

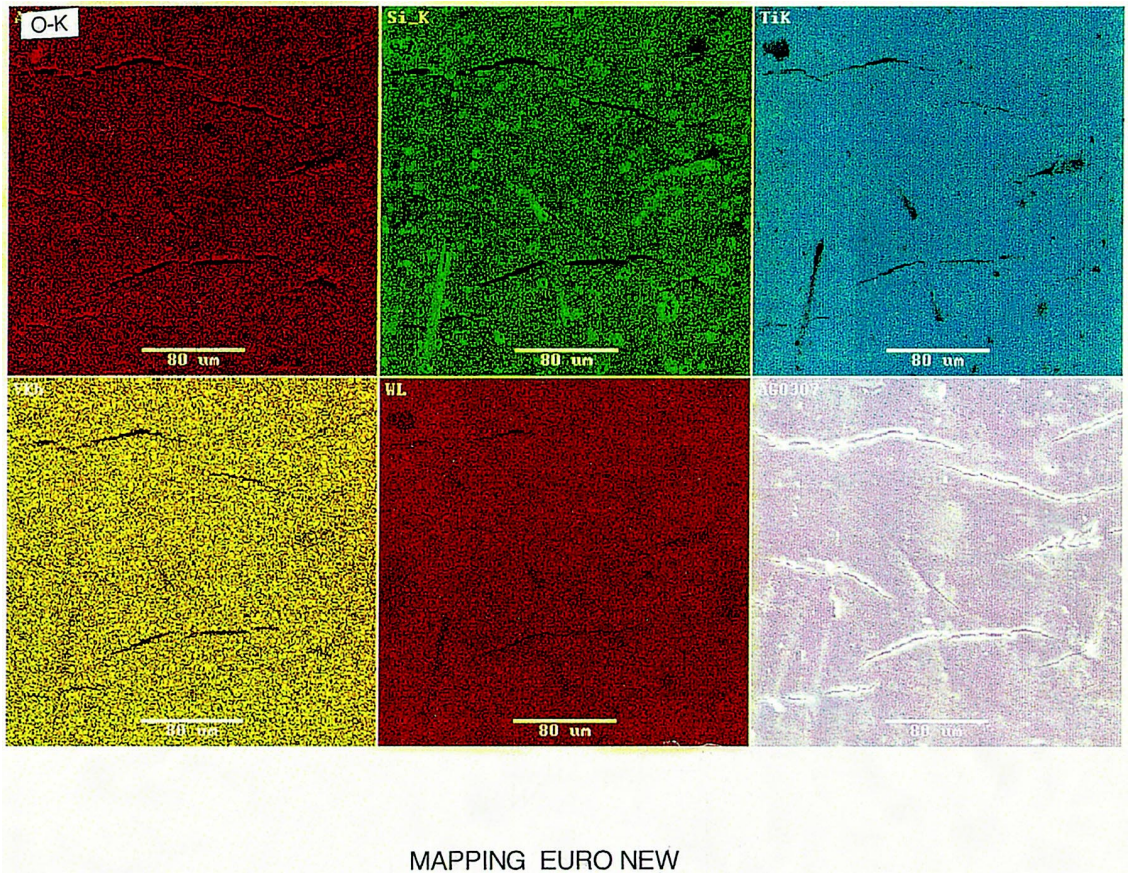


Fig. 7. SEM picture of the fresh sample (a) and mapping pictures for Si, Ti, O, V and W elements from EDX–SEM microprobe imaging.

2.3. AFM

Samples in their monolith form were analysed using Park Scientific CP, AFM instrument with a 50 nm radius tip under ambient atmosphere and using the tapping mode.

3. Results

3.1. SEM

Observations of fragments of the monoliths with low magnification showed the presence of bright grains, cracks and fibres embedded in the materials (see Fig. 1). The fibres were cylindrical with mean diameter around 10 μm and lengths varying from 100 to 500 μm. They were arranged without preferential orientation. At higher magnification, the surface appears to be composed of small round or egg-shaped particles with size lower than 40 nm (Fig. 2). No significant differences are observed between the fresh and used samples, only cracks and fibres were more visible on the used sample.

After gentle grinding, agglomerates of various sizes and constituted of the same particles as above were observed. The fibres appeared broken as individual fragments.

Figs. 3 and 4 give the distribution of the chemical composition from EDX analyses (expressed as atomic percentage of cationic elements) measured all along the fragments of the fresh and used monoliths. At a macroscopic scale, i.e. using observation areas of 1.44 and 0.16 cm^2 (42 analyses), the samples were fairly homogeneous. The narrowest distribution was observed for the W element for both fresh and used

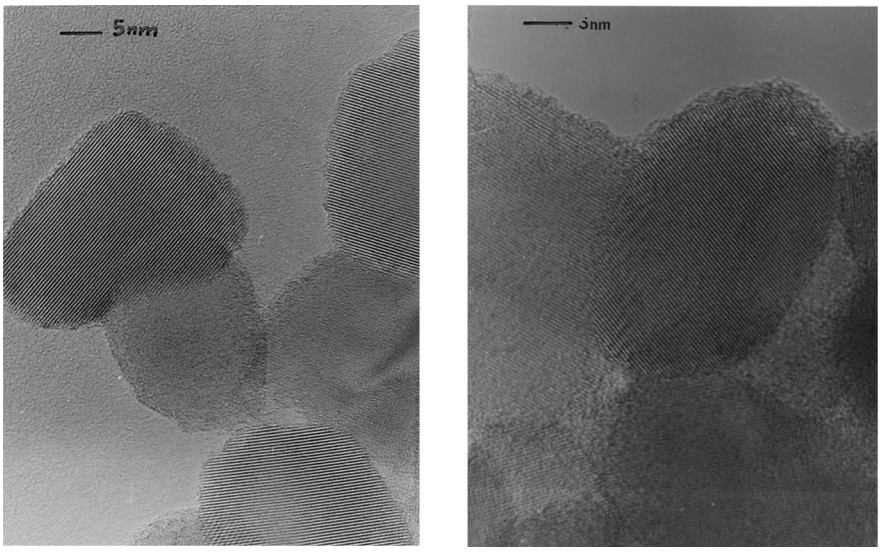


Fig. 8. High resolution TEM images of the fresh V_2O_5–WO_3/TiO_2 EUROCAT sample after gentle grinding.

samples, whereas the distribution for Ti and V elements was slightly broader and did not vary between fresh and used samples. On the contrary, distributions for Si and Ca were the broadest and increased with use in SCR process.

The average compositions did not vary markedly between fresh and used samples, except that of the used sample where the presence of sulphur was detected. Mean compositions and standard deviations are reported in Table 1 and are compared to those obtained by chemical analysis.

It is striking to note the low Si, Ca and Al contents observed by SEM analysis suggesting that the fibres, composed of Si, Ca and Al, are covered with a thick layer of V_2O_5–WO_3/TiO_2, i.e. actually embedded in the catalyst itself.

Comparison of fresh and used samples showed slight variations of the distribution for Ti and W (contents decreased) and Si and Ca (contents increased) indicating an erosion of the surface and the release of some fibres.

Observations at a mesoscopic scale, using the EDX-microprobe, strongly support this interpretation (Figs. 5 and 6). The used sample was more heterogeneous, with large discrepancies for the Ti and Si compositions. The higher Si compositions associated with higher Ca composition and lower Ti, W and V compositions were always observed on the fibres.

Table 1
Average contents (at.%) determined at different locations of three different monoliths fragments[a]

Samples	Analysis	Atomic composition (%)					
		Ti	Si	W	V	Ca	S
Fresh	SEM	85.8±0.6	7.2±0.4	3.7±0.3	2.8±0.3	0.6±0.2	n.d.
	EDX	81±4	14±5	3.0±0.3	1.9±0.6	n.d.	n.d.
	Chemical	77	14.3	3.1	2.9	2.7	0.5
Used	SEM	84.2±0.9	7.8±0.6	3.4±0.3	2.7±0.3	1.1±0.4	0.9±0.3
	EDX	79±7	16±7	3±0.7	1.9±0.6	n.d.	n.d.
	Chemical	77	14.4	3.1	3.0	2.2	0.8

[a] Observation plages: 1.44 or 0.16 cm^2.

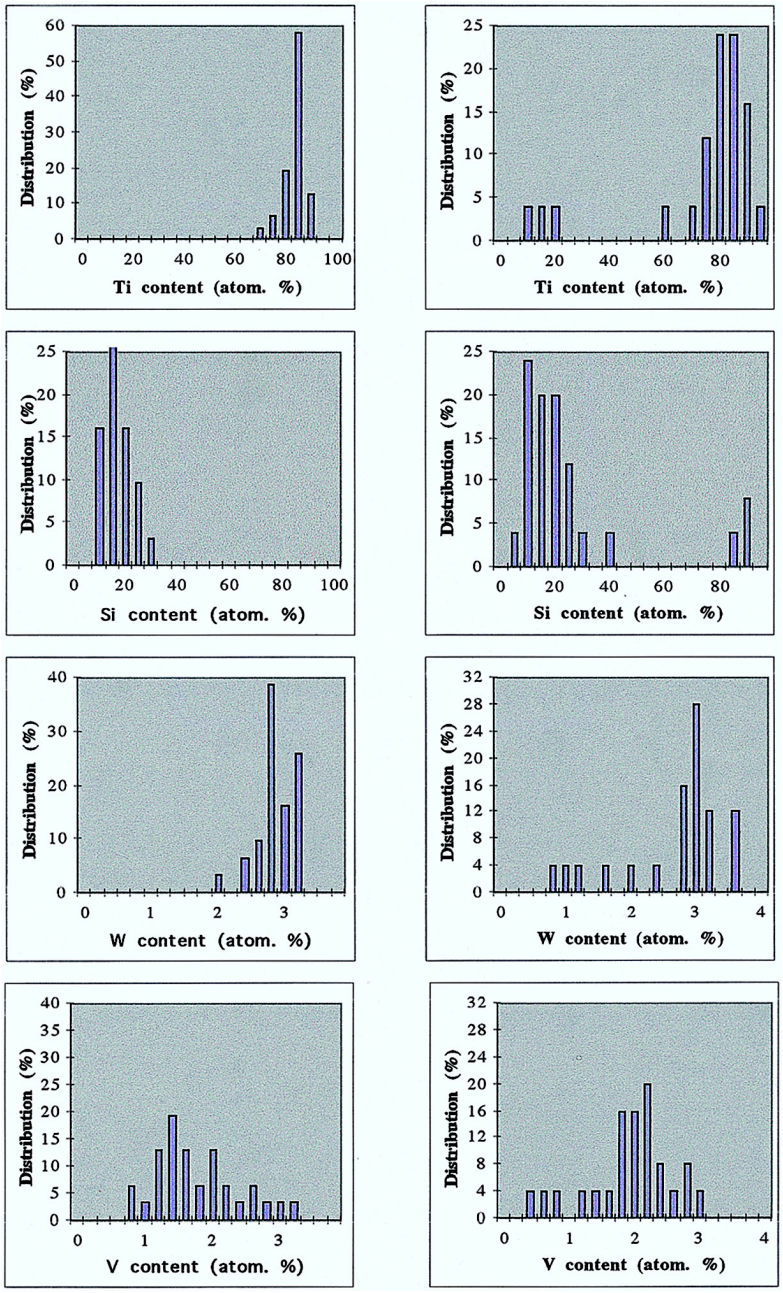


Fig. 9. Distribution of Ti, Si, W and V elements (at.%) for the fresh sample (left) and the used sample (right) determined by EDX–TEM analysis.

The bright grains were rich in S and Ca elements and the regions containing cracks were slightly richer in Ti, V, W and poorer in Si and Ca than the mean compositions.

Chemical analyses showed the presence of 0.8 at.% S in the used samples but also in lower amount (around 0.5 at.%) in the fresh sample. As no S was observed by SEM on the fresh sample, one may suggest that

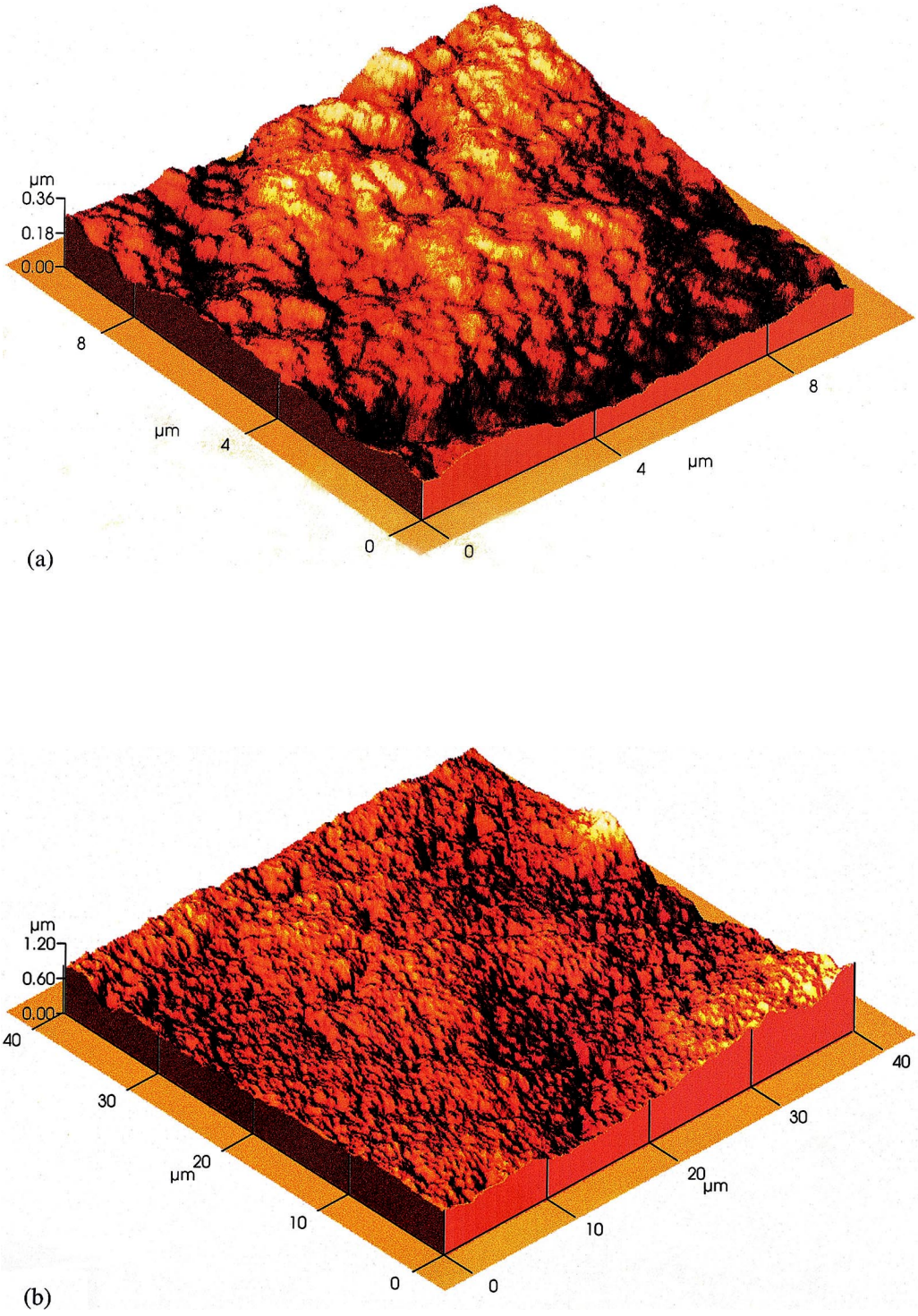


Fig. 10. AFM pictures at different scales for the fresh (a, b) and used (c, d) samples.

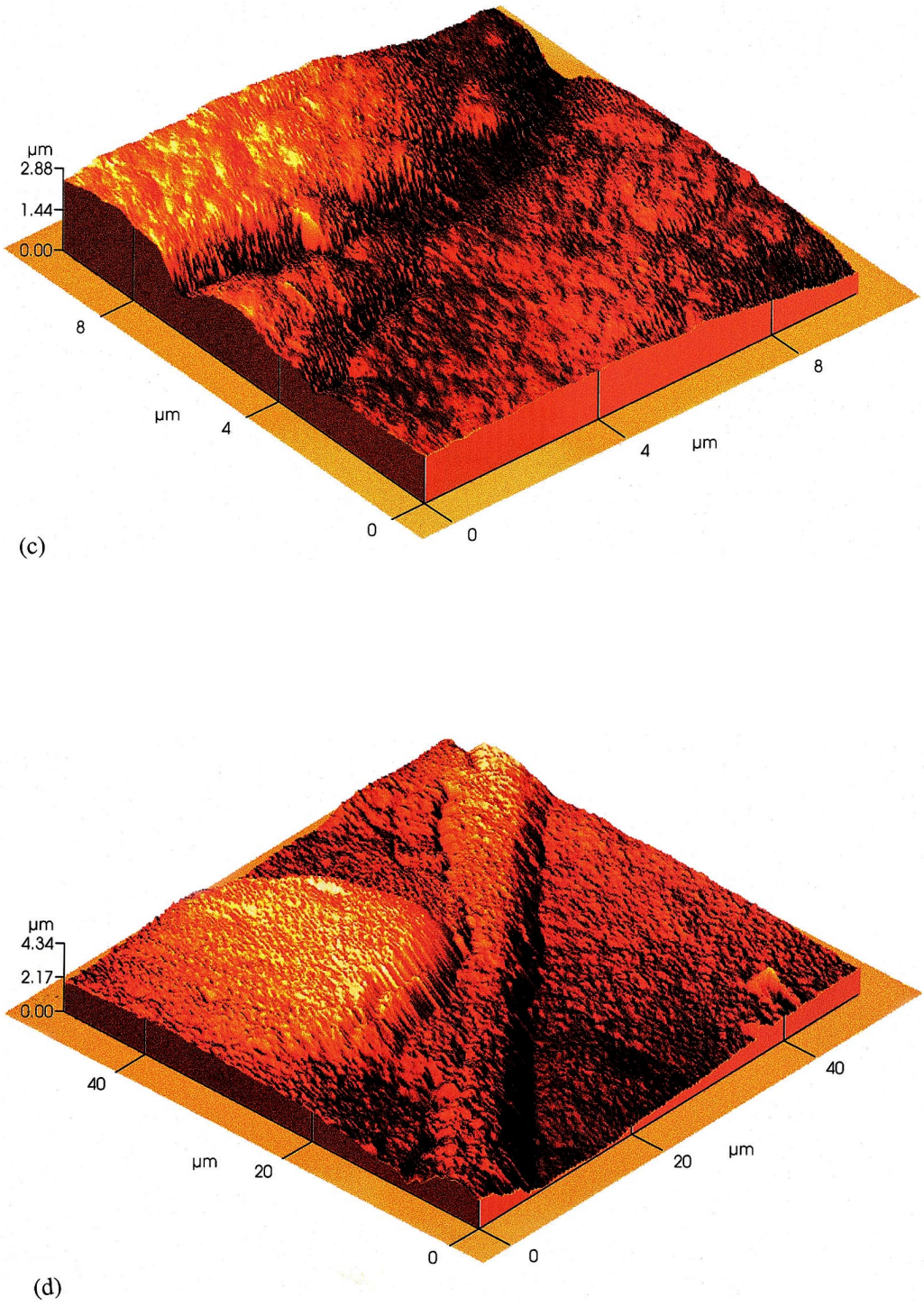
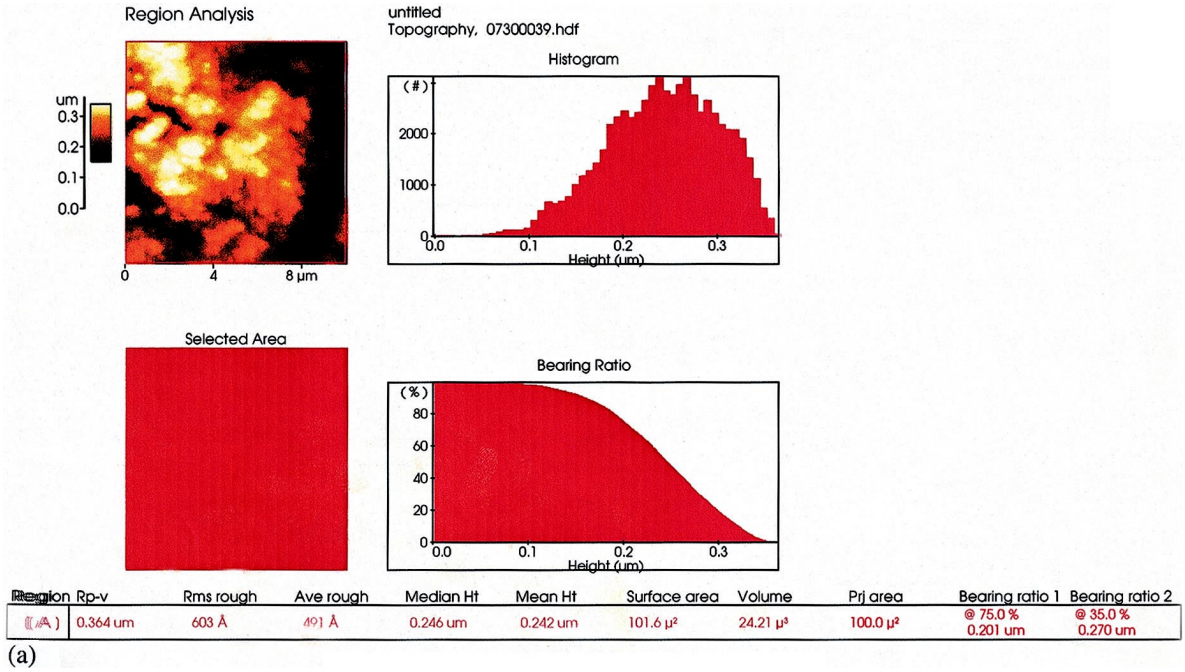
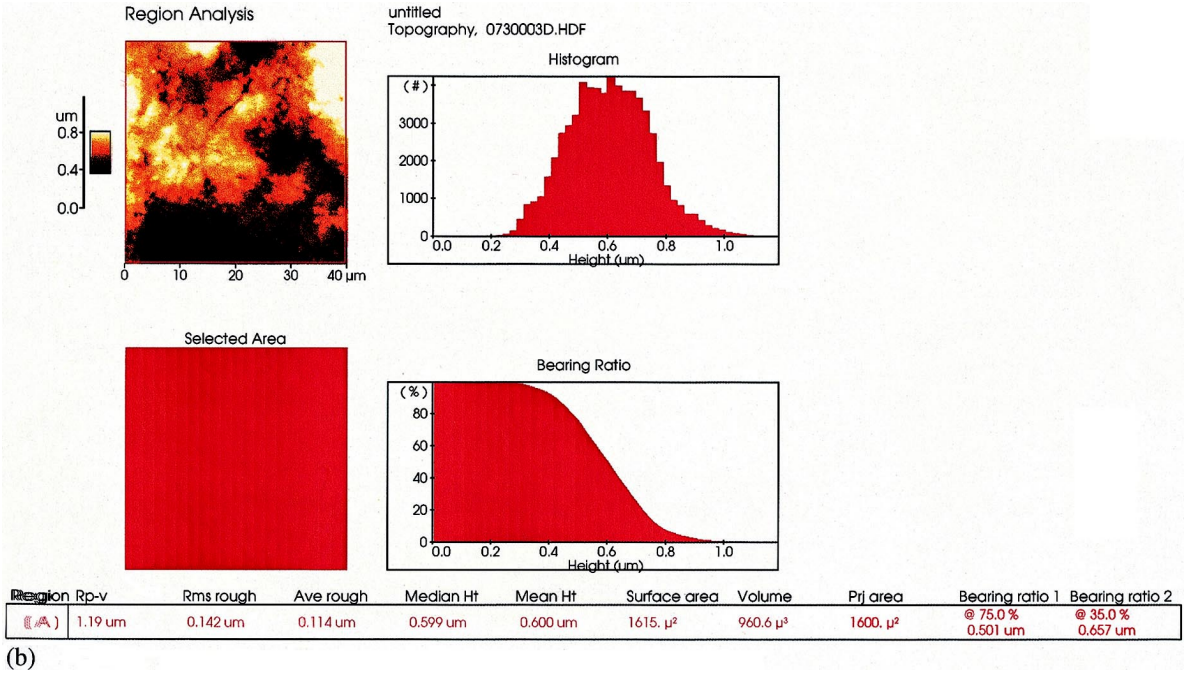


Fig. 10 (*Continued*).

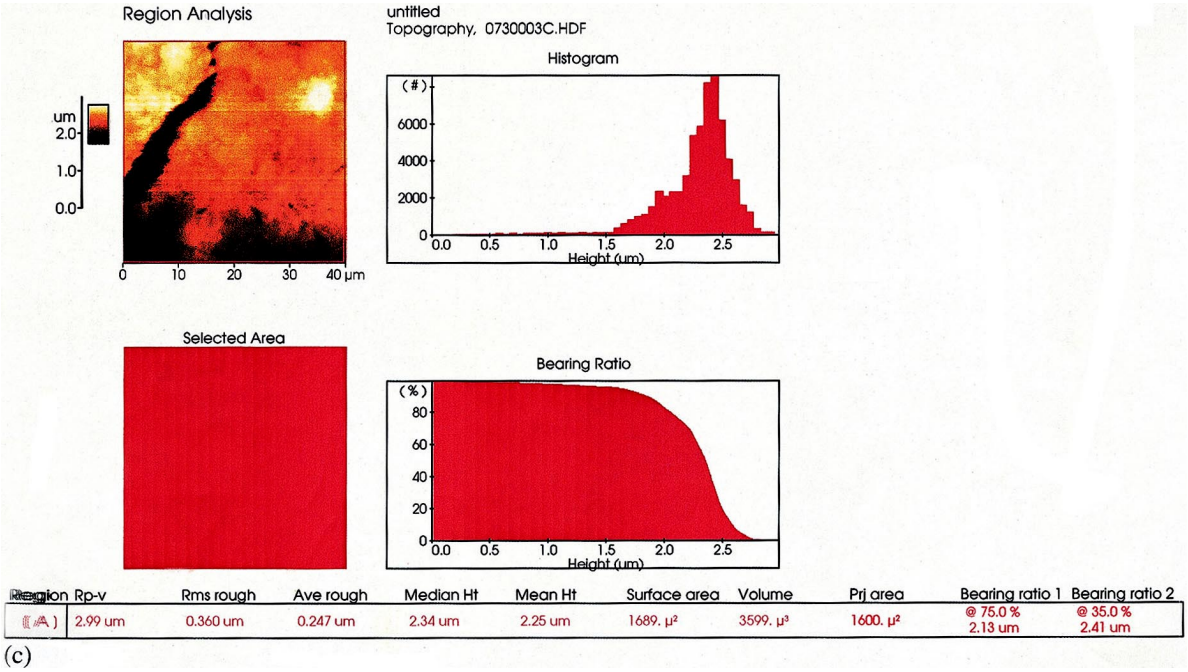


(a)



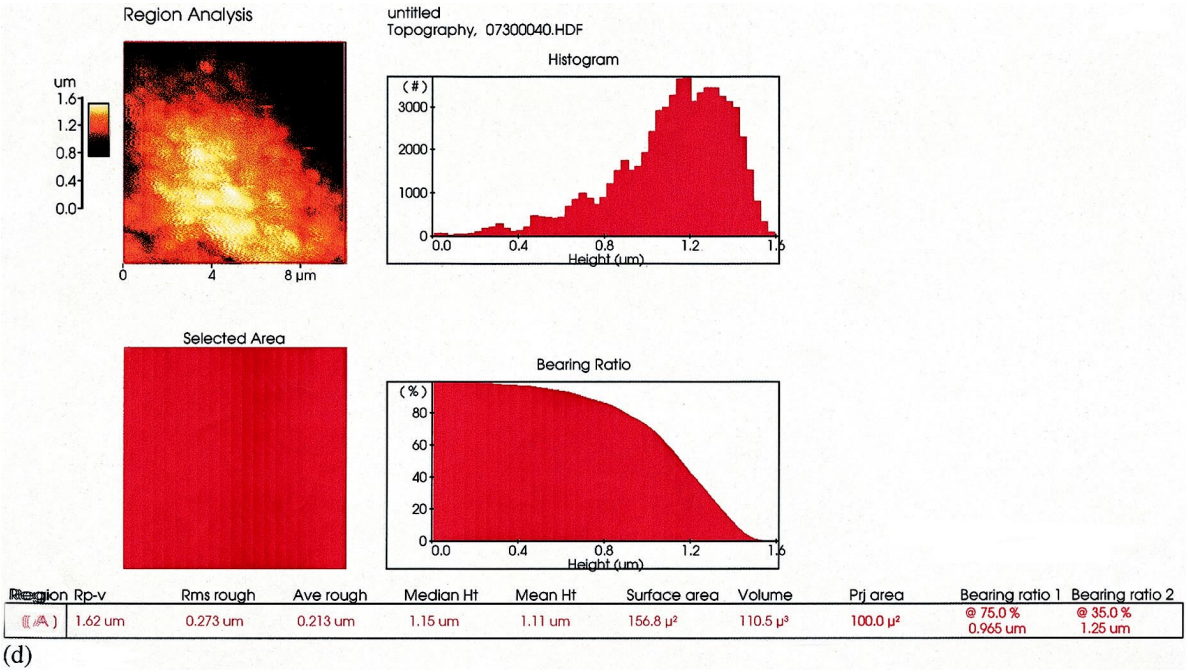
(b)

Fig. 11. Topological histograms of different regions of pictures from Fig. 10 for the fresh (a–c) and used (d–f) samples.



Region	Rp-v	Rms rough	Ave rough	Median Ht	Mean Ht	Surface area	Volume	Prj area	Bearing ratio 1	Bearing ratio 2
(A)	2.99 um	0.360 um	0.247 um	2.34 um	2.25 um	1689. µ²	3599. µ³	1600. µ²	@ 75.0 % 2.13 um	@ 35.0 % 2.41 um

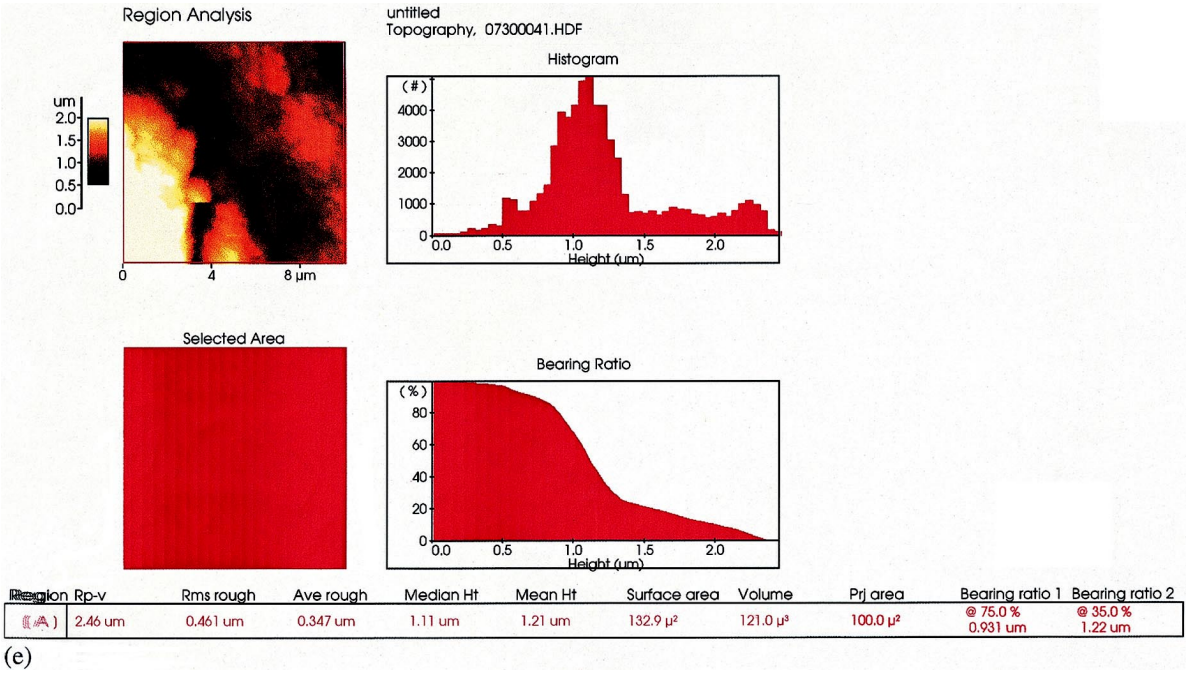
(c)



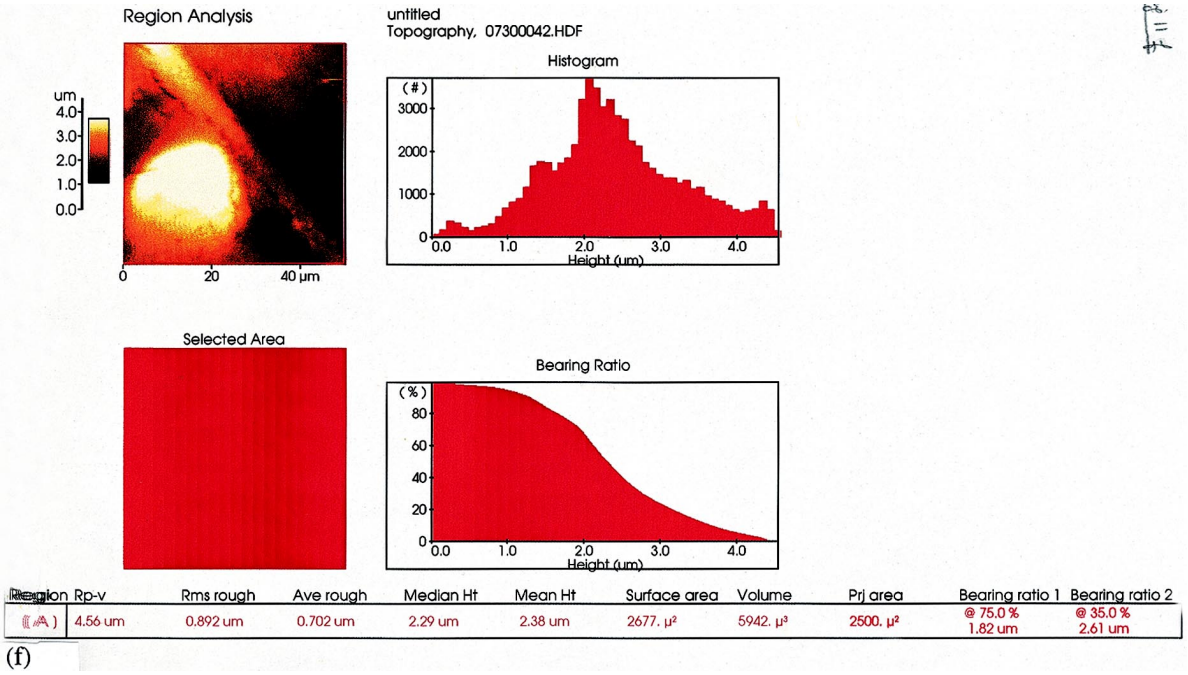
Region	Rp-v	Rms rough	Ave rough	Median Ht	Mean Ht	Surface area	Volume	Prj area	Bearing ratio 1	Bearing ratio 2
(A)	1.62 um	0.273 um	0.213 um	1.15 um	1.11 um	156.8 µ²	110.5 µ³	100.0 µ²	@ 75.0 % 0.965 um	@ 35.0 % 1.25 um

(d)

Fig. 11 (*Continued*).



(e)



(f)

Fig. 11 (*Continued*).

the S species were in the form of sulphate anions well dispersed on the support and that the new S species produced during the SCR process were deposited as calcium sulphate particles on the surface of the monolith and perhaps also as lead sulphate since Pb was detected by XPS (see Chapter 9).

The mapping by EDX–SEM of the fresh monolith is illustrated on Fig. 7. On the picture (Fig. 7a), cracks and some needles underneath can be observed. It appears from the Si mapping that the light regions, i.e. the highest Si concentrations, correspond to the fibres. Ti, V and W elements were observed regularly everywhere, except on the cracks (dark areas), while V was less regularly detected. Some higher O concentrations were detected on the edges of the cracks.

3.2. HRTEM and EDX–HRTEM

The two samples were found in the form of egg-shaped particles of homogeneous size around 20–30 nm by 30–40 nm. They were arranged in aggregates, with thickness depending on the grinding. Exceptionally, platelets with larger sizes 140–160 nm by 170–250 nm were observed.

An external surface area of ca. $50\,m^2\,g^{-1}$, i.e. very close to that obtained by the BET method ($47–46\,m^2\,g^{-1}$), was calculated assuming that the most frequent particles were equivalent to spheres with a mean radius of 15 nm deduced from electron microscopy and using a density value of $3.94\,g\,cm^{-3}$.

Fig. 8 clearly shows three different interference patterns for the particles. The most frequent spacings with d=0.357 nm corresponded to the (1 0 1) plane of the TiO_2 anatase phase and the other two with d=0.168 and 0.242 nm, probably to the (2 1 1) and (0 0 4) planes of TiO_2. Thus, the morphology of the anatase phase was somewhat different from that observed for the EL10V1 sample, which contained preferentially the (1 0 1) planes [1].

Note also an important feature in Fig. 8, namely that all particles had a thin amorphous layer on their periphery of two or three atomic spacings. This layer was slightly larger for the used sample. Over 20 analyses the amorphous layer thickness was estimated to be of 0.9 (±0.1) and 1.0 (±0.1) nm for the fresh and used samples, respectively.

A large number of particles and ensembles of particles were analysed by EDX–TEM to determine the Ti, W, V and Si contents. The distributions of these elements are given for the fresh and used samples in Fig. 9, the averages and the standard deviation values (calculated without the extreme values) being reported in Table 1.

As compared to SEM analyses on monolith surfaces, the distributions of Ti and Si are broader (especially for the used sample). However, the mean values were, for these elements, closer to the chemical ones. This confirms that the fibres were embedded in V_2O_5–WO_3/TiO_2.

On the used sample, some particles rich in Si were detected with W/Ti and V/Ti atomic ratios four to five times higher than the mean values and exceptionally large particles very rich in Ti but relatively poor in W and V were also detected (W/Ti and V/Ti atomic ratios being three to four times lower than the mean values). This may indicate that upon grinding the used samples, some W and V species are more easily separated from TiO_2 than from the phase rich in Si. However, one cannot exclude an artefact due to the grinding.

3.3. AFM

The topographic pictures at different scales are shown in Fig. 10a and b for the fresh (N) sample and Fig. 10c and d for the used (O) one. The histograms of selected areas are shown in Fig. 11a–c for the fresh (N) sample and Fig. 11d–f for the used one. The roughness in different selected area of the picture is given in Table 2.

It is worth noting that the roughness of the used sample is much larger than that of the fresh one, as if the catalyst had become more porous. No other modifications could be seen with more precision since a tip of 50 nm radius was used, which lead to a lower limit on the observations on the surface topography.

Table 2
Roughness of the fresh and used samples deduced from AFM study

Observation field (μm)	Roughness RMS (μm)	
	Fresh sample	Used sample
10	0.0603	0.273
50	0.360	0.461
50	0.142	0.892

4. Conclusions

These studies both by SEM on the surfaces of the monoliths and by TEM on the powders obtained by gentle grinding allow one to obtain more complete understanding of the V_2O_5–WO_3/TiO_2 EUROCAT catalyst. It is clearly observed that the catalyst was constituted of a lattice of fibres, containing the Si, Al and Ca elements, presumably from bentonite, coated with the TiO_2 anatase phase, containing the W and V elements. This phase is composed of small particles of homogeneous size, nicely crystallised, as shown by the interference fringes of the (1 0 1) and (2 0 0) planes of anatase in the TEM pictures.

An important observation was made, namely that the periphery of all well crystallised TiO_2 particles was amorphous within two or three atomic spacings (ca. 0.9 nm), which may play a determining role in catalytic properties. This amorphous layer was slightly larger (ca. 1.0 nm) for the used sample.

The W content appeared homogeneously distributed both by SEM and TEM, whereas the V content was less homogeneously distributed, especially at a microscopic scale, but no pure V_2O_5 particles could be detected in agreement with the absence (or presence at very low concentration) of crystallised V_2O_5 crystallites as shown by the XRD study (see Section 2).

During the SCR process, the coating was somewhat altered and some more fibres were detected as shown by higher Si contents in SEM imaging and by an increase of the roughness in AFM. On the other hand, new S species appeared on the surface of the monolith which are probably calcium and/or lead sulphates. The mean chemical compositions, of both fresh and used samples did not vary appreciably, as determined both by SEM and TEM, while the distributions of Ti and Si are strongly broadened and, at the microscopic scale, in some cases, a small segregation could be observed between TiO_2 anatase phase and W and V species.

Reference

[1] M. De Boer, Catal. Today 20 (1994) 97.