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A STEM-HAADF study of the distribution of vanadium atoms in the Mo-V-Te-O M1 phase

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Multicomponent molybdates based catalysts are among the most promising catalysts for light alkanes oxidation or ammoxidation. The active phase of these catalysts, called *M1*, is a solid solution with the total formula $(AO)_{2-2x}(A_2O)_{2x}M_{20}O_{56}$ with $A=Te$ or Sb , $M=Mo, V$ and eventually Nb , and $0 < x < 1$.

The structure is built up from corner sharing octahedral forming channels where Sb or Te cations are located (see figure 1a). The respective occupation level of the octahedra sites by Mo , V and Nb can vary with the composition of the phase or the preparation method [1]. If these occupation levels do not alter the crystal structure, they have a significant impact on the activity and selectivity of the catalyst. X-ray diffraction using the Rietveld method is the main technique used to determine these occupation levels but it appeared difficult to ascertain several conclusions reached. For example the site $S5$ was proposed to be partially occupied by vanadium in one study and not in another [2,3]. Discrepancies also exist on the occupation or not of the heptagonal channels of the structure by Te or Sb cations.

In this work high-resolution high-angle annular dark-field technique (HAADF STEM) was employed to characterize the *M1* phase, with the aim of quantifying the occupancy of sites mentioned previously.

The technique has already been used on these phases to investigate the location of Ta when it was substituted to Nb in the structure, or to characterize the Sb containing *M1* phases [4, 5]. The *M1* phase studied here contained tellurium and no niobium. It was prepared with a new method using a keplerate $\{Mo_{132}Te\}$ ammonium salt precursor dissolved with vanadyl sulfate in an aqueous solution, and submitted to a hydrothermal treatment at $175^\circ C$ for 24h [6]. The solid was filtered, washed with water and dried with ether. Samples for TEM observation were cut using an ultramicrotome.

According to the physics of incoherent electron scattering as collected in HAADF imaging, the intensity of atomic columns resolved in the experimental micrographs is expected to be directly linked to the nature of atoms present in these columns:

$$I_{HAADF} = \sum Z_i^{\alpha}$$

where Z_i is the atomic number of chemical specie i , and α an exponent varying between 1.6 and 2 [7].

From this relationship, integrating the intensities of dots imaging atomic columns, after a background subtraction, gives the basis of a quantitative analysis of the chemical content of each column. This can be done using a parametric model [8] or directly from the images, with a normalization procedure performed on columns of known composition (if any). We apply a similar strategy to see whether the occupancy of V -containing sites can be quantified. Experiments were conducted on a 300 kV TITAN-FEI, probe C_s -corrected microscope, installed at Minatec, CEA, Grenoble. Figure 1 illustrates briefly the results. Fig. 1 b-c) refer to a sample, the composition of which was analyzed by EDX and further determined according to our quantitative analysis of HAADF intensities: both chemical compositions (regarding cations) are in very good agreement, i.e. $Mo_{0.80}V_{0.16}Te_{0.04}$ for EDX and $Mo_{0.81}V_{0.16}Te_{0.03}$ for HAADF. This method will be explored in order to understand the discrepancies encountered in the literature on site occupancies [9].

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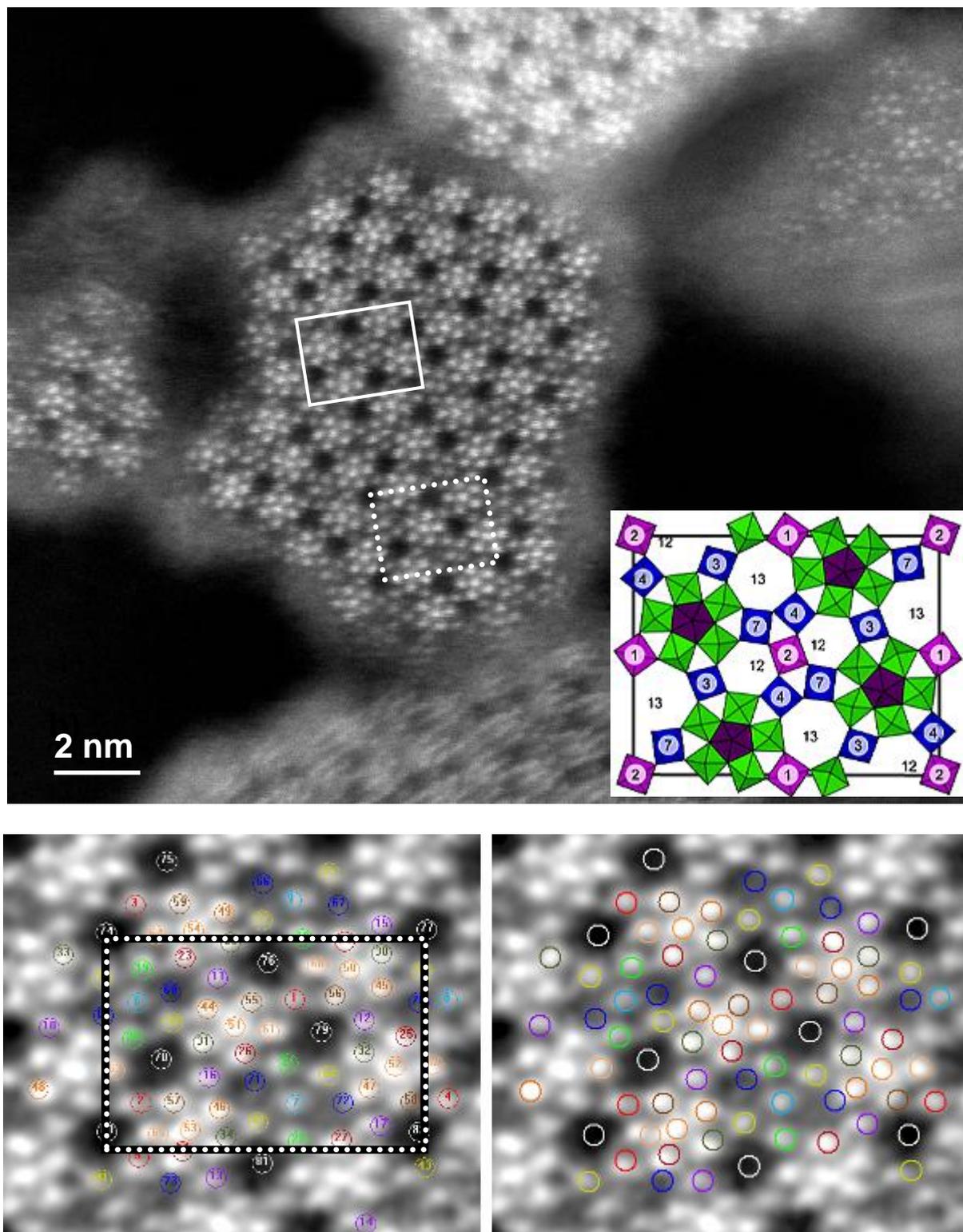


Figure 1. STEM-HAADF imaging of the Mo-V-Te-O *M1* phase. a) Low mag image showing a crystallite close to the [001] orientation; the unit cell is shown in insert (space group $Pba2$, with $a = 2.112$ nm, $b = 2.659$ nm [3] as underlined in the micrograph; the dotted frame refers to fig. b)). b) Detail (from another crystal) showing the starting ideal atomic positions from the crystallographic model (columns of interest for the statistical analysis of intensities are numbered). c) Refined positions (after running a 'peak search' routine) used for intensity integration, leading to the quantitative chemical analysis reported in the text.