Phosphorus promoted WS_2/Al_2O_3 catalysts studied by transmission electron microscopy

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A series of WS_2/Al_2O_3 catalysts containing a varied amount of phosphorus (0.0, 2.5 and 6.0 wt% P_2O_5), sulfided at two different temperatures (873 and 1073 K), were studied by means of high-resolution transmission electron microscopy (HRTEM). The stacking of (002) layers in the WS_2-2H crystallites of the "rag" structure increases with the addition of phosphorus, whereas its length is kept almost constant. At high sulfidation temperatures phosphorus shows a stabilizing effect on the catalysts by retarding the stacking growth of WS_2 crystallites. Additionally, an aluminum phosphate crystalline phase is identified in the phosphorus promoted catalysts.

Keywords: phosphorus-containing catalysts; tungsten disulfide; high-resolution electron microscopy

1. Introduction

Molybdenum disulfide and tungsten disulfide are well known catalysts used for hydrotreating processes like hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) [1,2]. The catalytic activity of these materials increases notoriously by using promoters as nickel or cobalt, which contribute to generate a synergistic effect in these catalysts (Ni–Mo, Ni–W). In order to explain the synergistic effect, several theories have been proposed based on: the intercalation model [3], the electronic effect [4], the presence of a mixed phase [5] and the remote control model [6].

In recent years, intense research has been devoted to studying the effect of phosphorus as secondary promoter in Co(Ni)–Mo/Al_2O_3 hydrotreating catalysts. Phosphorus addition facilitates catalyst preparation and usually enhances HDN, hydrodemetallation (HDM) and hydrogenation (HN) activity of catalysts [7,8].

Although a clear understanding of its role in catalysis has not yet been achieved, several explanations have been proposed to account for the improvement in activity due to phosphorus, such as: an improved dispersion of the Mo and Ni (Co) active phases [9,12], a change in Mo dispersion and the coordinatively unsaturated Mo sites [8], the influence of phosphates on the hydrogenolysis step [13], the increased stacking of MoS_2 and change of morphology [14], a modification in the properties of the Mo and Co edge sites [15], a change in acidity [10], and the formation of new sites associated with phosphate [16].

Even though many industrial hydrotreating catalysts are based on tungsten, very little attention has been paid to the influence of phosphorus on W based catalysts. The exception are the works by Atanasova et al. [17,18] who studied by X-ray diffraction (XRD) and different spectroscopies (diffuse reflectance, X-ray photoelectron spectroscopy and IR spectroscopy) the effect of phosphorus on the structure of oxidic P–Ni–W/Al_2O_3. More recently, in a previous work, we reported the effect of phosphorus on the structural and catalytic properties of WS_2/Al_2O_3 catalysts sulfided at 673 K for the simultaneous HDS/HDN of gas oil and pyridine [19]. It was detected by high-resolution transmission electron microscopy (HRTEM) the influence of phosphorus on the WS_2 slabs, which represent the catalytic sites of these reactions.

In order to obtain further insight about the role of phosphorus and temperature in tungsten disulfide based catalysts, in this work we study by means of HRTEM the microstructure of the same series of WS_2/Al_2O_3 catalysts as a function of the phosphorus concentration at the range of sulfidation temperatures of 873 and 1073 K. This technique has revealed to be very useful for the study of the structure of layered sulfides [20–24].

2. Experimental procedure

A series of alumina supported catalysts containing a constant amount of tungsten (20 wt% WO_3) and various loadings of phosphorus (0.0, 2.5, and 6.0 wt% P_2O_5) were prepared by wet coimpregnation of γ-Al_2O_3 with aqueous solution of orthophosphoric acid and ammo-

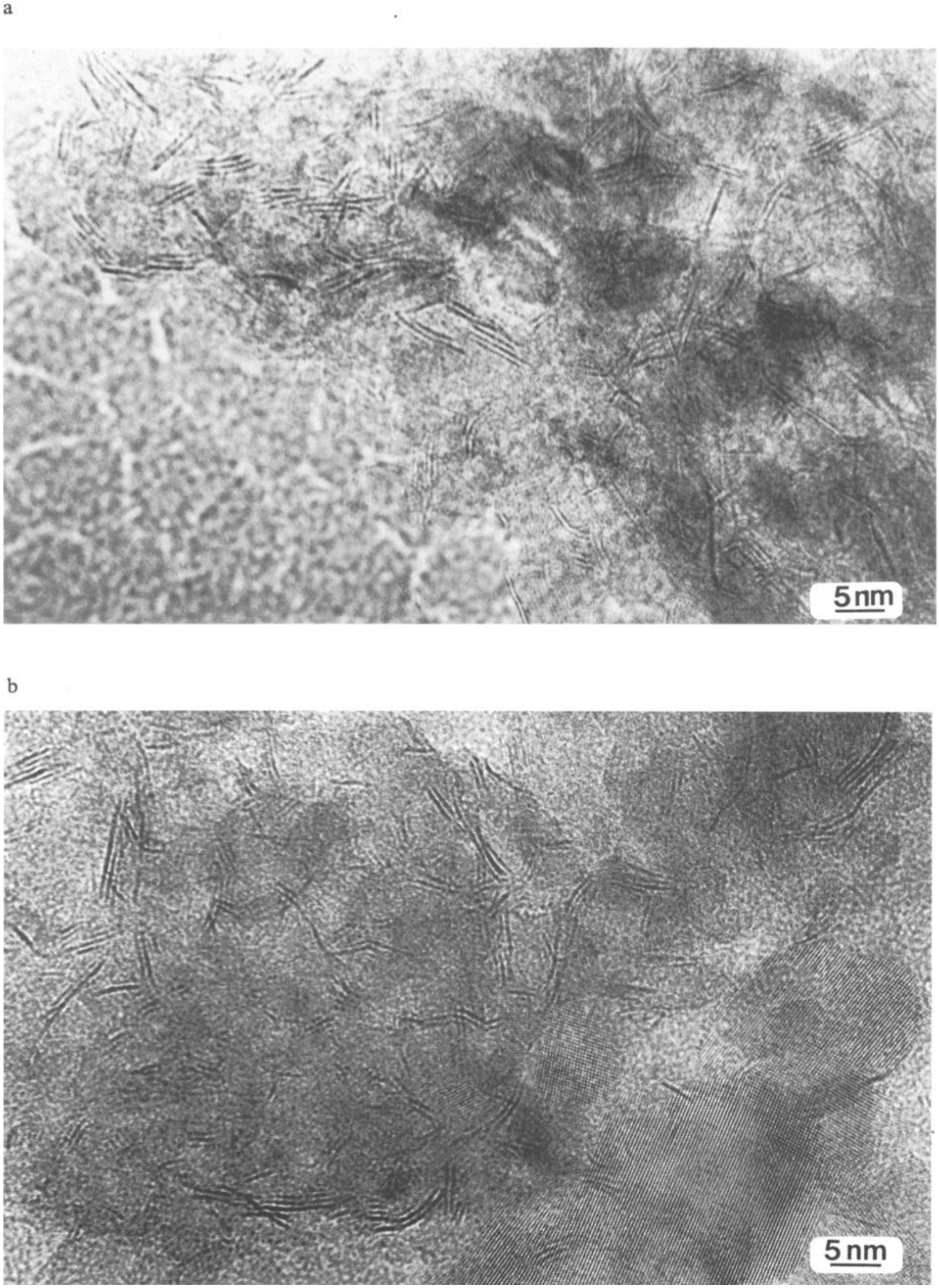

Fig. 1. Typical high-resolution micrographs of WP(*x*) catalysts sulfided at 873 K and with different phosphorus concentrations. (a) WP(0.0), (b) WP(2.5) and (c) WP(6.0). In all cases we identify the typical (002) WS_2-2H planes (0.62 nm) forming groups with various nnmbers of layers and lengths of the "rag" structure. (Continued on next page.)

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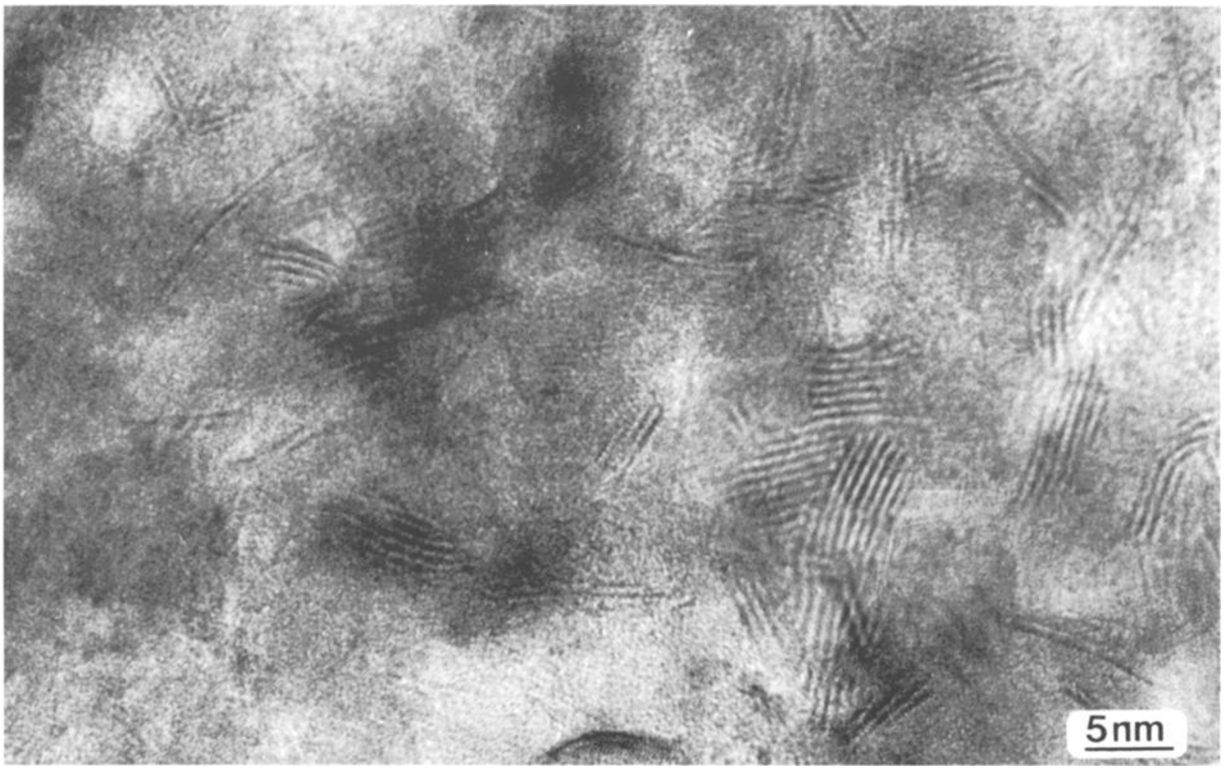

Fig. 1. (Continued.)

nium metatungstate in a rotary evaporator. The γ-Al_2O_3 used is Girdler T-126, which has a surface area 188 m^2 g^{-1}, a pore volume 0.39 cm^3 g^{-1}, and particle size 0.15–0.25 mm. The impregnation solutions were adjusted to a pH of 1.5 by the addition of nitric acid solution, when necessary. The value of $pH = 1.5$ is slightly lower than that corresponding to the solution with the highest phosphoric acid content used. The impregnated samples were dried at 393 K for 8 h and calcined, first, at 653 K in flowing air for 2.5 h, and then, at 823 K in static air for 4.5 h. Then, the catalysts were sulfided with 20 vol% H_2S/H_2 mixture at 873 and 1073 K for 4 h. Sulfided samples were finally ground in *n*-heptane, ultrasonically dispersed and were kept in *n*-heptane. The catalysts are denoted WP(x), where x is the weight percentage of P_2O_5.

HRTEM measurements of the sulfided catalysts were performed with a Jeol 4000EX microscope. A drop of each catalyst in suspension was placed on a copper grid coated with carbon film for its observation in the microscope. Several micrographs of each sample were analyzed and statistics of the number and length of WS_2-2H crystallites were obtained.

3. Results

In figs. 1a–1c we present three representative high-resolution micrographs of the WP(x) catalysts with ($x = 0.0, 2.5$ and 6.0 wt% P_2O_5), sulfided at 873 K. In all cases we identify the typical (002) WS_2-2H planes (0.62 nm) of the "rag" structure, forming stacks with various numbers of layers and lengths. Statistics on the number (N) and length (L) of the (002) planes were performed on several micrographs of each catalyst sample. For each sample, about 100 stacks were measured and the results are summarized in figs. 2a and 2b. We observe that the maximum frequencies of appearance for N and L change as a function of the phosphorus concentration. The catalyst WP(6.0) shows larger N and broader distribution than catalyst WP(0.0) (fig. 2a). Similar results are observed for L, as catalyst WP(6.0) presents longer L than catalyst WP(0.0) (fig. 2b). In both cases, WP(2.5) shows an intermediate value between WP(0.0) and WP(6.0).

In figs. 3a–3c, we show three representative high-resolution micrographs of the WP(x) catalysts, sulfided at 1073 K, with $x = 0.0$, 2.5 and 6.0 wt% P_2O_5, respectively. We observe that tungsten disulfide crystallites in all catalysts appear to be more highly stacked and longer, as compared to samples sulfided at 873 K. In figs. 4a and 4b we present the statistics of N and L for the catalyst at 1073 K. The maximum frequencies of appearance as well as the size distributions of N and L are a function of the phosphorus concentration at this temperature, similarly to the case at lower temperatures. For higher concentrations of phosphorus, N and L are larger and broader.

In table 1, we present average values of N and L, for all catalysts, calculated by the formula $N, L = \sum(N_i, L_i * F_i)/\sum F_i$. In table 1 results from ref. [19] for

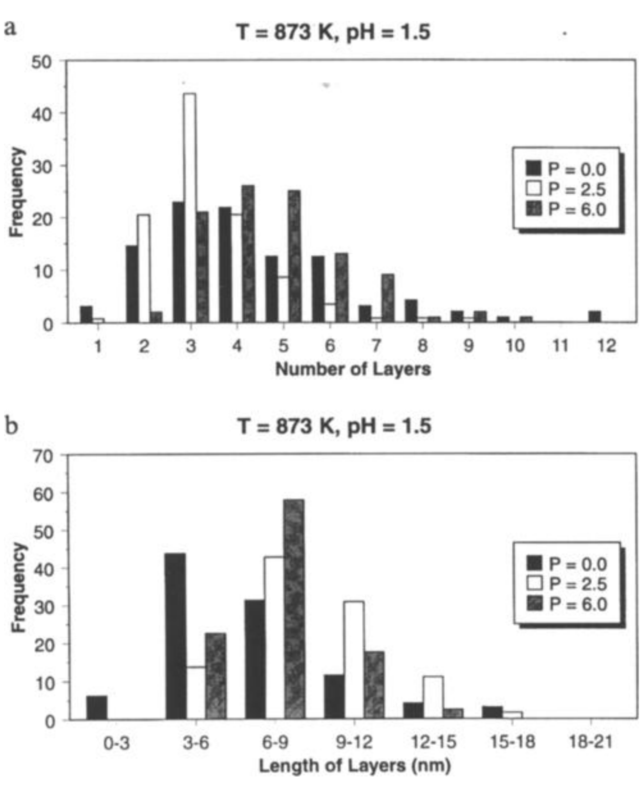

Fig. 2. Distribution of: (a) number of layers (N) and, (b) length (L) of layers (nm), of WS_2 crystallites at 873 K.

samples sulfided at 673 K are also included. For samples without phosphorus, WP(0.0), the value of N increases as a function of temperature. This trend in N is also found on samples with phosphorus, WP(2.5) and WP(6.0), but within a minor variation of stacking. In these samples, for higher temperatures, relatively lower increments are observed (see fig. 4a). The values of L are also temperature dependent, and larger increments are observed for catalysts WP(6.0) (see fig. 4b).

In addition to the "rag" structure of WS_2-2H usually found in this type of catalysts, other well resolved lattices were also visible for phosphorus containing samples. Identification of such structures was possible by measuring interplanar spacing and angles, and matching against the cards in the JCPDS files. As an example of these other phases, we show in fig. 5, for sample WP(6.0) sulfided at 873 K, an area (marked as "A") identified as a hexagonal form of $Al(PO_3)_3$ ($a = 1.09$ nm, $c = 0.92$ nm). Planes measuring 0.34 nm and with an angle of 82° were identified as ($3\ -1\ -1$) and (022) planes in that structure (JCPDS No. 15-364). Another example is the $AlPO_4$ crystalline phase found in a previous work [19].

In fig. 6 we show a high-resolution micrograph of WP(0.0) sulfided at 673 K showing an area with the tungsten oxide structure (JCPDS No. 36-102). The existence of this plane is also supported by XPS measurements performed on these samples [25], where it is shown that

a

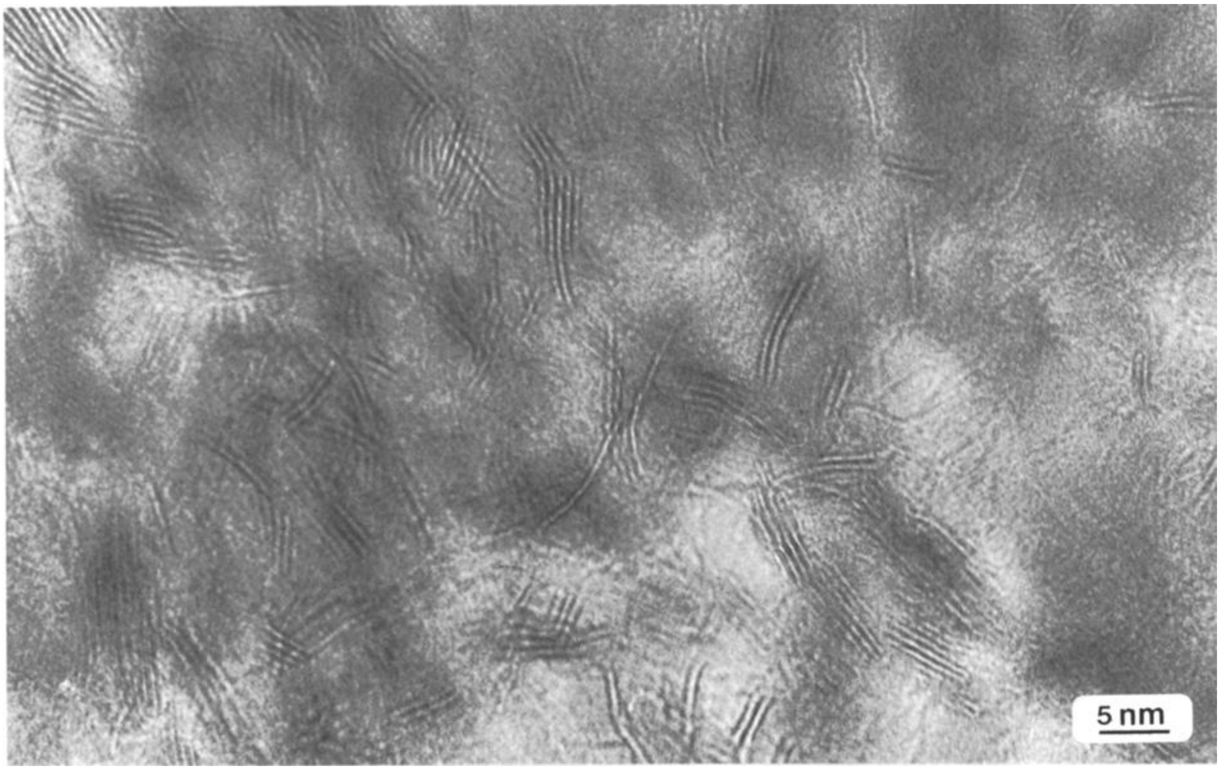

Fig. 3. Typical high-resolution micrographs of WP(x) catalysts sulfided at 1073 K and with different phosphorus concentrations. (a) WP(0.0), (b) WP(2.5) and (c) WP(6.0). In all cases we identify the typical (002) WS_2-2H planes (0.62 nm) forming groups with various numbers of layers and lengths of the "rag" structure. (Continued on next page.)

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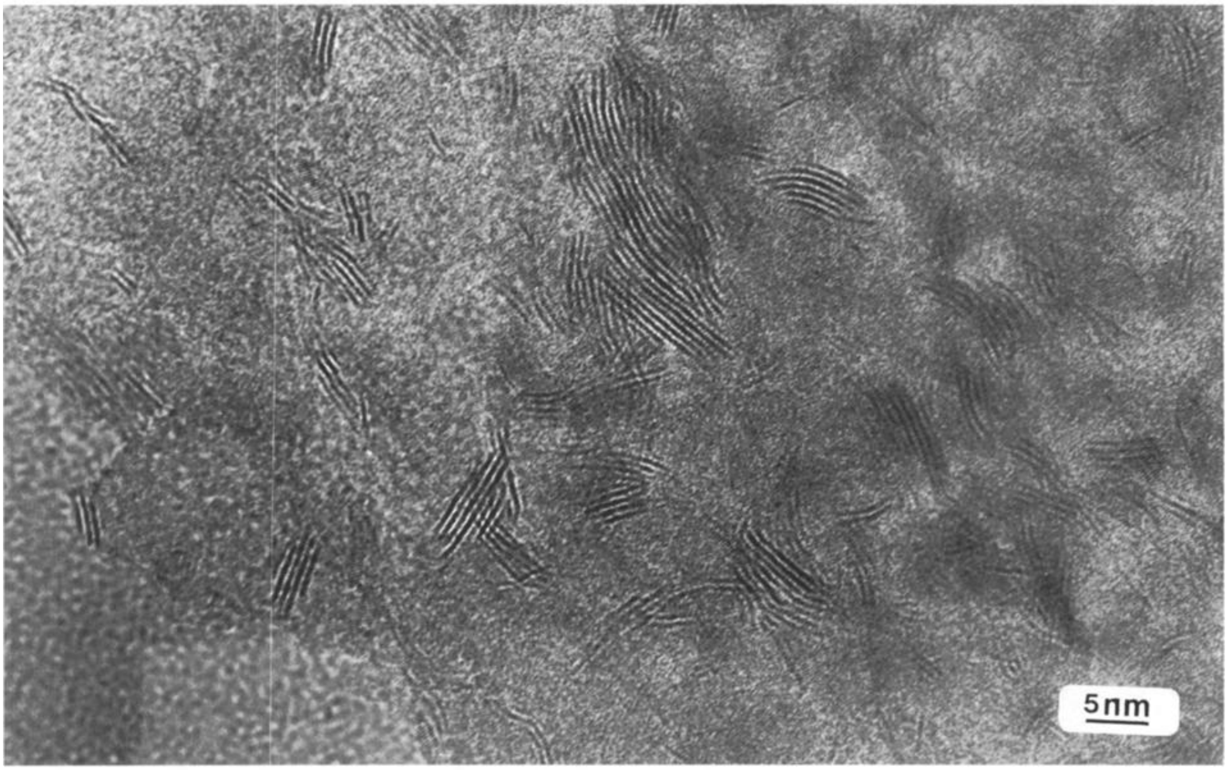

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Fig. 3. (Continued.)

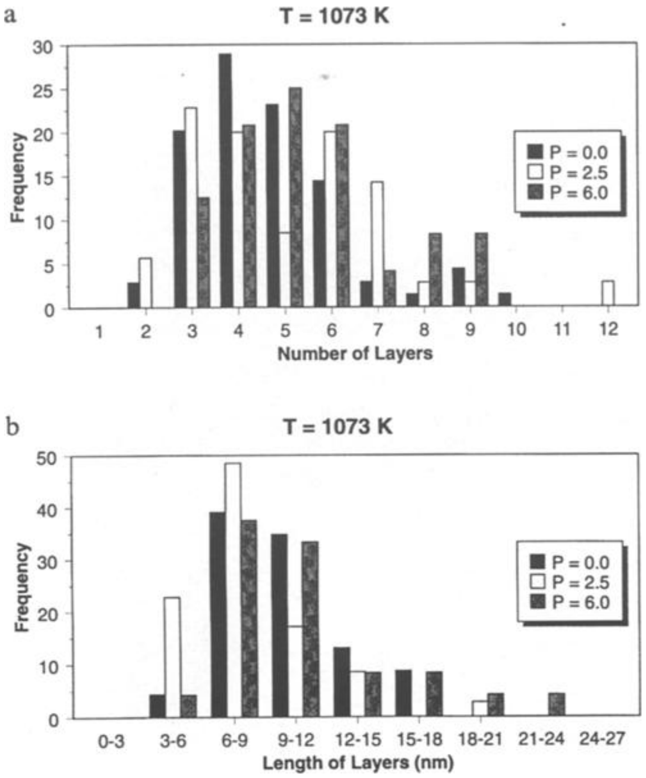

Fig. 4. Distribution of: (a) nnmber of layers (N) and, (b) length (L) of layers (nm), of WS_2 crystallites at 1073 K.

tungsten oxide concentration is larger for catalysts sulfided at 673 K than those sulfided at 873 or 1073 K.

4. Discussion

The stacking and length of WS_2 crystallites, measured by HRTEM, generally increase with phosphorus content as well as with sulfidation temperature, the significance of the variation depending on phosphorus concentration and temperature range. The main effect of phosphorus seems to be to increase the stacking of layers as a function of phosphorus concentration at each temperature, and is more noticeable for samples sulfided at 673 K and 873 K. The lower effect of phosphorus for samples sulfided at 1073 K can be attributed to the fact that, at this temperature, the unpromoted sample has suffered an extensive sintering, and then, the relative increase of the stacking of layers due to the presence of phosphorus appears small.

Table 1
Statistics of the length (L) and number (N) of (002) WS_2-2H planes, for WP(x) catalysts sulfided at different temperatures, from HRTEM measurements. Results from catalysts sulfided at 673 K were obtained from ref. [19]

Catalyst	Temp. (K)	N	L (nm)
WP(0.0)	673	2.1	6.3
WP(2.5)	673	3.4	6.1
WP(6.0)	673	4.4	6.5
WP(0.0)	873	4.3	6.2
WP(2.5)	873	3.5	8.7
WP(6.0)	873	5.0	7.5
WP(0.0)	1073	4.5	9.6
WP(2.5)	1073	5.1	8.1
WP(6.0)	1073	5.4	10.9

The stacking increase for all temperatures as a function of phosphorus concentration, suggests that this phenomenon is related to a preparation step which is temperature independent, like impregnation. Thus, the phosphorus induced stacking increase could be explained by a change in the distribution of tungsten species at the alumina surface as a consequence of the presence of phosphoric acid during impregnation. In a similar case to fluoride ions in tungsten supported on F-modified alumina catalysts [24,26], phosphate ions have a larger affinity than tungstate ions for the alumina Al^{3+} ions, diminishing the available sites for tungsten adsorption. At very high phosphorus content (6.0 wt%) tungstate ions that are not adsorbed proceed to form surface polytungstates and as a result, during calcination, these species produce segregation of WO_3 clusters. The surface polytungstates (octahedral W) are more easily reduced than the monomeric tetrahedral WO_4^{2-} species since the W^{6+} ions of the former are surrounded by a lower number of Al^{3+} ions, and consequently, are less polarized. Changes in the nature of the oxidic precursor species would lead to changes in the architecture of the WS_2 crystallites obtained after sulfidation.

The crystallite length (L) is only slightly affected by phosphorus concentration at a given temperature. On the other hand, L is affected by temperature. Between 673 and 873 K a small increase is noted, then at 1073 K, a significant effect is observed. The length increase or lateral growth of MoS_2 crystallites as a function of sulfidation temperature is due to diffusion of crystallites onto the substrate, followed by sintering among them through edge planes [27]. Such mechanism is mainly due to the high reactivity of edge (lateral) planes. Lateral growth at high temperatures is believed to be favored in phosphorus containing samples due to the presence of crystalline phosphate phases, which allow faster diffusion of crystallites as compared to alumina.

Phosphorus also induces an augment in surface sulfidation as revealed by XPS due to an increase of the WS_2/WO_x ratio [25]. The low degree of sulfiding and the relatively small size of WS_2 crystallites with low stacking of phosphorus free catalyst is a consequence of the high concentration of W^{6+} tetrahedrally coordinated species which are very stable as mentioned above. In other words, it can be expected that an increase in polytungstates, and consequently, an increase of catalyst reducibility with phosphorus loading will result in increased

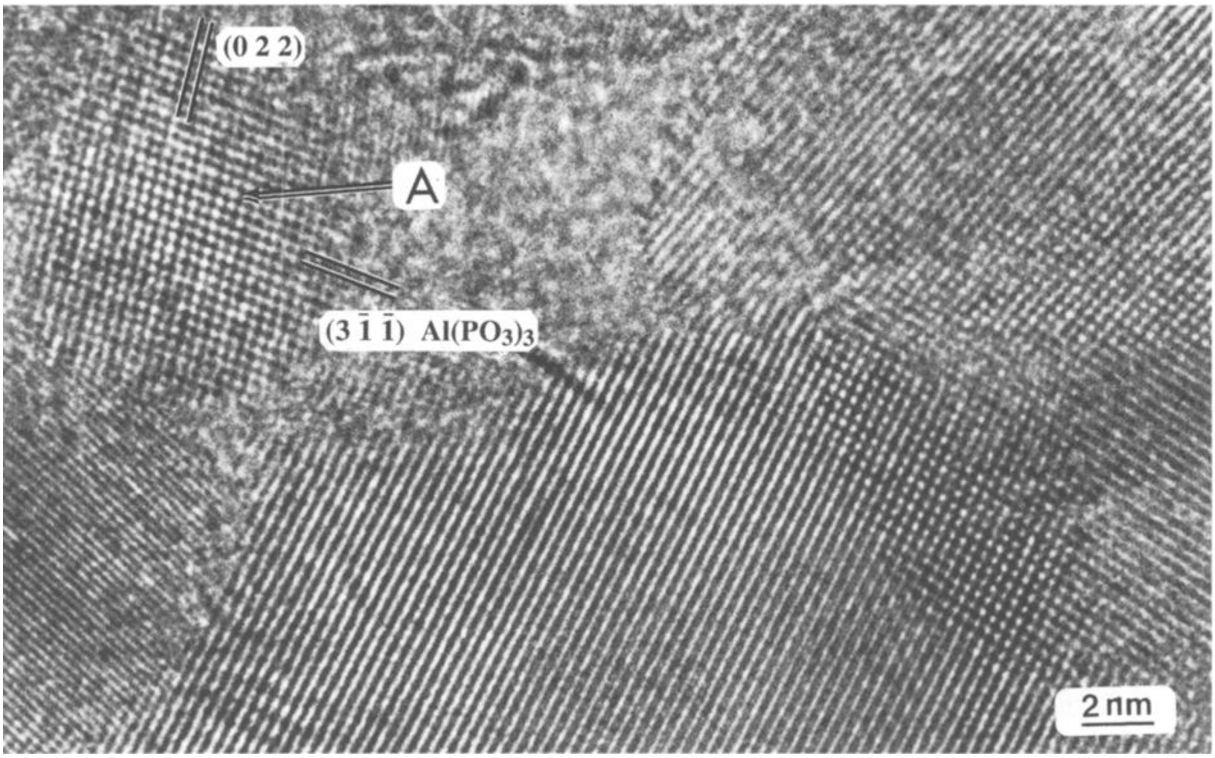

Fig. 5. High-resolution micrograph of WP(6.0) catalyst, sulfided at 873 K, showing an aluminum phosphate phase, where the area marked as "A" is a hexagonal form of $Al(PO_3)_3$ ($a = 1.09$ nm, $c = 0.92$ nm), and the planes measuring 0.34 nm and with angle of 82° are identified as the (3 −1 −1) and (022) planes in that structure.

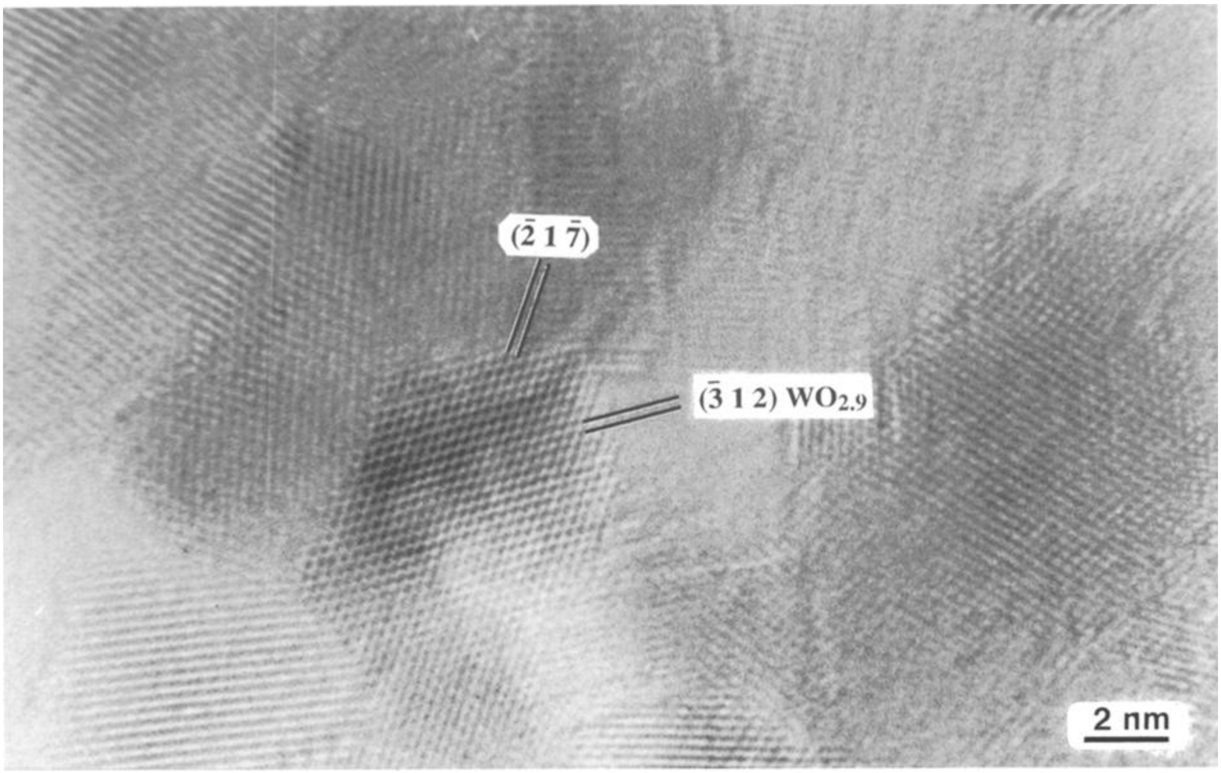

Fig. 6. High-resolution micrograph of WP(0.0) sulfided at 673 K showing a crystal identified as tungsten oxide.

sulfidation, which should favour the formation of larger WS_2 crystals and higher stacking.

5. Conclusions

The variations observed by HRTEM in the phosphorus containing catalysts, indicate that phosphorus plays an important role on defining the morphology of WS_2 crystallites in these catalysts. From our results of the series of WS_2/Al_2O_3 catalysts containing phosphorus (0.0, 2.5 and 6.0 wt% P_2O_5), sulfided at two different temperatures (873 and 1073 K), and characterized by means of HRTEM, the following conclusions can be obtained.

The stacking of (002) layers in the WS_2-2H crystallites of the "rag" structure increases with the addition of phosphorus. This effect is larger at 673 K and not so noticeable at 873 and 1073 K. On the other hand, the length of (002) layers is mainly modified by temperature, while phosphorus gives only minor changes. Variation of stacking is believed to occur by formation of polytungstates during impregnation. Crystallite growth, which affects their length, is related to thermal sintering through edge planes.

Additionally, aluminum phosphate crystalline phases are identified in the phosphorus promoted catalysts.

Further studies related to the evaluation of the catalytic activity, textural properties, XPS spectroscopy and X-ray diffraction are in progress.

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