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Morphology and composition of NiMoW/P-Al_2O_3 systems based on the modified support with varied P_2O_5 content

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1. XPS Spectral Measurements.

The binding energy (BE) scale of the spectrometer was preliminarily calibrated using the position of peaks corresponding to the Au $4f_{7/2}$ (83.96 eV) and Cu $2p_3/2$ (932.62 eV) core levels of pure metallic gold and copper. The samples were mounted on a holder using double-sided adhesive tape. In the case of non-conductive samples, the Kratos charge neutraliser system was used, and the spectra were charge-corrected to provide the C 1s spectral component of adventitious carbon (C–C and C–H) at 284.8 eV. In addition to the survey photoelectron spectra, the narrow spectral regions (Al 2p, S 2p, S 2s, Mo 3d, W 4f, C 1s, O 1s, and Ni 2p) were also recorded. The pass energy of analyser was 160eV for the survey spectra and 40 eV for the narrow scans. The individual spectral regions were analyzed in order to determine the BE of peaks, to identify the chemical state of elements, and to calculate the relative ratios of elements on the catalyst surface.

Examples of spectral decomposition for the PNiMoW/Al_2O_3 catalysts are shown in Figures S1 and S2. The XPS decomposition provided the absolute quantification of each species:

$$C(j)_T(\%) = \frac{A_j/S_j}{\sum_{i=1\ldots n} A_i/S_i} \cdot 100,$$

wherein A_i is the measured area of species i, S_i is the sensitivity factor of atom related to species i (provided by the manufacturer), and $C(j)_T$ is the absolute content of species j.

We determined the relative concentrations of formed species (Ni^{2+}, NiS, Ni(Mo)(W)S, Mo^{6+}, MoS_xO_y, MoS_2 , W^{6+}, WS_xO_y, and WS_2) for the each sulfided catalyst. Nickel-promoted tungsten sulfide (NiWS) or molybdenum sulfide (NiMoS) could not be isolated separately. The presence of bracketes in the Ni(Mo)(W)S phase designation suggests the existence of both NiMoS and NiWS phases and also of NiWS mixed phase. For example, the relative amount of Ni(Mo)(W)S was determined according to the following equation:

$$[Ni(Mo)(W)S](\%) = \frac{A_{NiMoWS}}{A_{NiMoWS} + A_{NiS} + A_{Ni^{2+}}} \cdot 100,$$

wherein A_X is the peak area of species X.

The effective Ni content in Ni(Mo)(W)S phase was determined using the following equation:

$$C_{Ni(Mo)(W)S} = [Ni(Mo)(W)S] \cdot C(Ni)_T$$

wherein $C(Ni)_T$ is the effective concentration of nickel determined by XPS (wt%).

The absence of any signal at 169.0eV (characteristic of sulphates) indicated that the sulfided catalysts were not reoxidised during the transfer of solids from the sulfiding reactor to the XPS instrument.

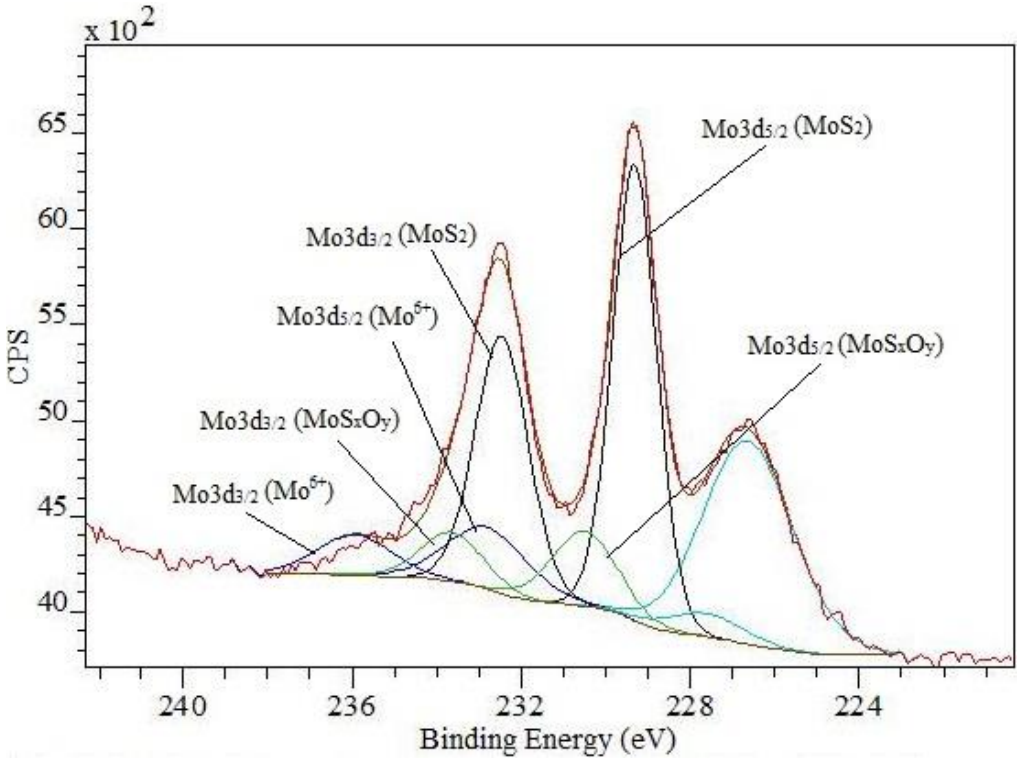


Figure S1 Mo 3d spectra recorded for PNiMoW/Al_2O_3 catalysts.

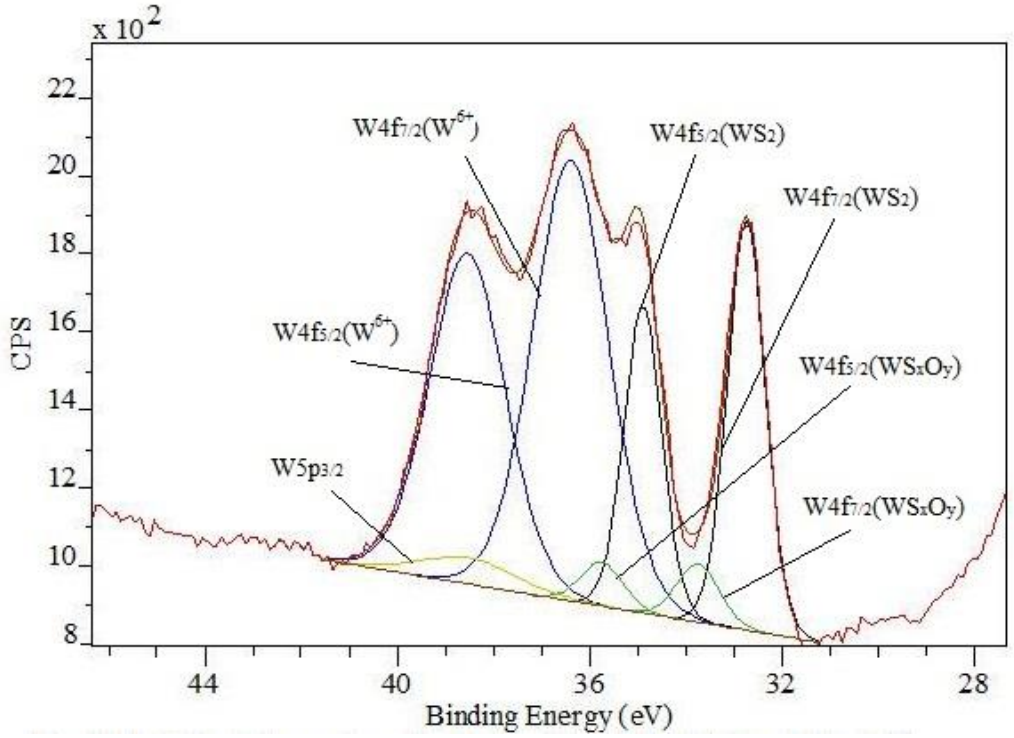


Figure S2 W 4f spectra recorded for PNiMoW/Al_2O_3 catalysts.

2. High Resolution TEM Imaging.

HRTEM images of catalysts were obtained on a Tecnai G220 electron microscope with a 0.14 nm lattice-fringe resolution and an accelerating voltage of 200 kV. The high-resolution images of periodic structures were analysed using the Fourier method. Local energy-dispersive X-ray analysis (EDXA) was carried out on an EDXA spectrometer fitted with a Si(Li) detector with a 130 eV resolution. The HRTEM samples were prepared on a perforated carbon film mounted on a copper grid, and 10–15 representative micrographs were obtained for each the catalyst in the high-resolution mode. Typically, the lengths of at least 400 slabs were measured for each the catalyst.

The acquired TEM images (Figure S3) allowed us to obtain the main geometric parameters of active phase. The number of sites occupying the different locations on the molybdenum disulfide layers was calculated using the formulas given below:

$$\overline{L} = \frac{\sum l_i}{n}$$

$$\overline{N} = \frac{\sum n_i N_i}{n}$$

$$n_i^{/} = \frac{10 \times \frac{\overline{L}}{3.2} + 1}{2}$$

$$M_e = (6n_i^{/} - 12)\overline{N}$$

$$M_c = 6\overline{N}$$

$$M_T = (3n_i^{/2} - 3n_i^{/} + 1)\overline{N}$$

wherein $\overline{L}$ is the average slab length of NiMo(W)S_2 slabs, *n is* the total number of slabs, l_i is the length of slab *i*, $\overline{N}$ is the average stacking number of slabs, n_i is the number of stacks with N_i layers, $n_i^{/}$ is the number of Mo(W) atoms along one side ofslab, M_e is the number of Mo(W) atoms at the edge sites, M_c is the number of Mo(W) atoms at the corner sites, and M_T is the total number of Mo(W) atoms.

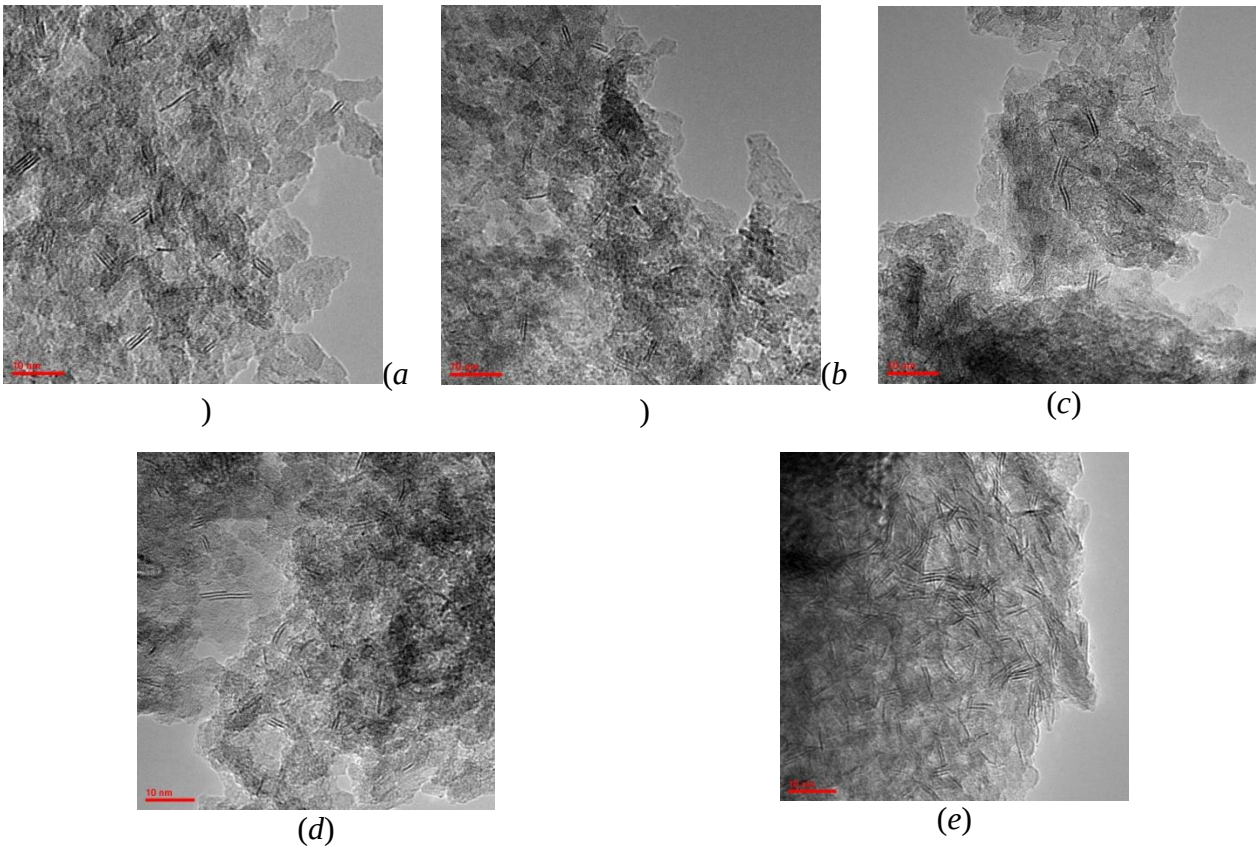
Assuming that the Mo(W)S_2 slabs were the perfect hexagons, the average fraction of Mo(W) atoms at the Mo(W)S_2 edge surface (*D*) was calculated in order to measure the extent of NiMoWS dispersion. This approach has been previously used in the investigations of promoted NiMoWS active phase. NiMoWS dispersion (*D*) was statistically evaluated by dividing the total number of Mo(W) atoms at the edge surface ($Mo(W)_e$), including corner sites ($Mo(W)_c$), by the

total number of Mo(W) atoms (Mo(W)T) using the slab sizes measured in the TEM micrographs:

$$D = \frac{(Mo+W)_e+(Mo+W)_c}{(Mo+W)_T},$$

wherein n_i is the number of Mo(W) atoms along one side of Mo(W)S_2 slab as determined by its length and t is the total number of slabs in the TEM micrograph.

Representative HRTEM micrographs of five sulfided NiMoW/P(0), NiMoW/P(0,5), NiMoW/P(1), NiMoW/P(2) and NiMoW/P(5) catalysts are shown below (see Figure S3).



(*a*) (*b*) (*c*)

(*d*) (*e*)

Figure S3 HRTEM micrographs of sulfided (*a*) NiMoW/P(0), (*b*) NiMoW/P(0,5), (*c*) NiMoW/P(1), (*d*) NiMoW/P(2), and (*e*) NiMoW/P(5) catalysts.