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Molecular approach to prepare mixed MoW alumina supported hydrotreatment catalysts using $H_4SiMo_nW_{12-n}O_{40}$ heteropolyacids

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Table 1: Intra HPA cation-anion bond distances (Å) after single crystal XRD diffraction of the two selected compounds. The multiplicity is also given.

β-$H_4[SiMo_3W_9O_{40}]$.10 H_2O; symmetry : tetragonal ; space group : P-4n2			
Si1	O21	2x	1.626(6)
	O24	1x	1.629(8)
	O23	1x	1.637(9)
W1	O11	1x	1.728 (9)
	O18	2x	1.910(6)
	O15	2x	1.923 (7)
	O24	1x	2.362(8)
W2	O2	1x	1.695(7)
	O12	1x	1.903(6)
	O18	1x	1.908(6)
	O9	1x	1.913(5)
	O6	1x	1.925(6)
	O23	1x	2.331(6)
W3	O1	1x	1.711(7)
	O12	1x	1.883 (6)
	O14	1x	1.919 (6)
	O17	1x	1.923(5)
	O8	1x	1.926(6)
	O21	1x	2.306(6)
W4	O13	1x	1.694(8)
	O22	1x	1.898 (2)
	O19	1x	1.904(5)
	O14	1x	1.919 (6)
	O10	1x	1.942 (6)
	O21	1x	2.349(6)
W5	O4	1x	1.699(7)
	O17	1x	1.905 (6)
	O19	1x	1.916 (6)
	O5	1x	1.929(5)
	O15	1x	1.933(7)
	O24	1x	2.362 (6)
Mo1	O3	1x	1.670 (7)
	O10	1x	1.870 (7)
	O16	1x	1.890 (2)
	O8	1x	1.924(6)
	O25	1x	2.006(7)
	O21	1x	2.389 (5)
Mo2	O7	1x	1.677(10)
	O25	2x	1.918(7)
	O6	2x	1.940 (6)
	O23	1x	2.368 (7)
α-$H_4[SiMo_1W_{11}O_{40}]$·30 H_2O; symmetry: monoclinic ; space group : $P2_1/m$			
Si1	O9	4x	1.624 (6)
W1|Mo1	O3	1x	1.670(6)
	O6	1x	1.79 (2)
	O2	1x	1.829 (8)
	O10	1x	1.993 (7)
	O5	1x	2.01 (2)
	O9	1x	2.386 (6)
W2|Mo2	O1	1x	1.67(1)
	O5	1x	1.81(2)
	O8	1x	1.827(9)
	O10	1x	2.014 (8)
	O7	1x	2.01 (1)
	O9	1x	2.408 (6)
W3|Mo3	O4	1x	1.66 (1)
	O2	1x	1.831(8)
	O8	1x	1.851 (9)
	O6	1x	1.96(2)
	O7	1x	1.98 (1)
	O9	1x	2.382 (6)

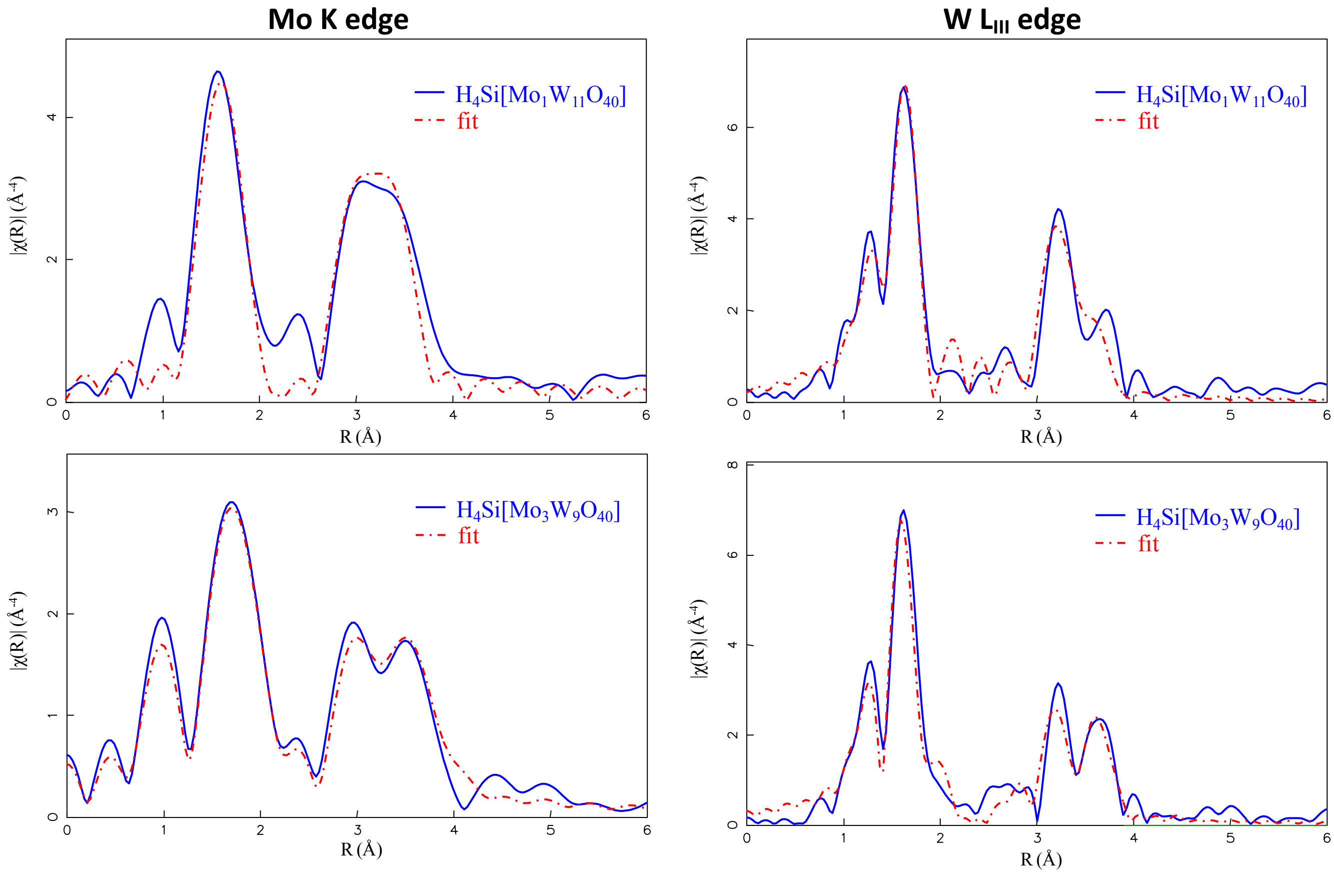

Figure 1. Magnitude of the Fourier transform of the Mo K-edge and W LIII edge spectra (solid line) and model (dotted line) for bulk $H_4Si[Mo_1W_{11}O_{40}]$ and $H_4Si[Mo_3W_9O_{40}]$ HPAs.

Infra-Red Spectroscopy

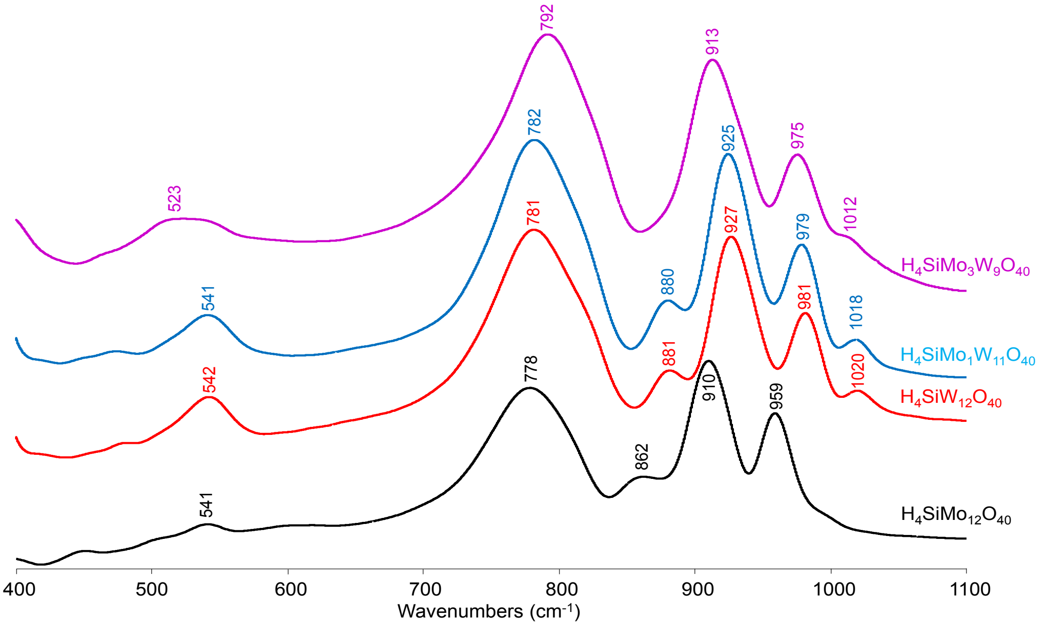

Figure 2. IR spectra of bulk HPA: comparison of mixed HPA with the monometallic ones

Fig. 2 presents IR spectra of $H_4[SiMo_1W_{11}O_{40}]$, $H_4[SiMo_3W_9O_{40}]$, $H_4[SiMo_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$. According to literature data on $SiW_{12}O_{40}$ IR characterization,[1,2] characteristic bands are assigned to the Keggin structure: Si-O and W=O_t vibrations stretching mode (t stands for terminal) are observed at 927 and 981 cm^{-1} respectively while lines at 880 and 781 cm^{-1} are assigned to W-O_b-W and W-O_c-W vibrations (O_b oxygen atoms between two octahedra of different W_3O_{13} groups and O_c, oxygen atoms between two octahedra from a same W_3O_{13} group) . In the low wavenumbers (520-540 cm^{-1}), vibrations are due to squeletal deformations of the Keggin unit. All these vibrations were observed in mixed heteropolyanions with small variations in wavenumber. The IR spectra of mixed HPA are very close and look like that of $H_4SiW_{12}O_{40}$ indicating that in the mixed HPA Mo- and W-oxygen vibrational modes cannot be observed separately. $H_4[SiMo_1W_{11}O_{40}]$ IR spectrum is also in agreement with that of $SiMoW_{11}O_{40}$ prepared as microtubes reported by Shen et al.[10]

Raman Spectroscopy

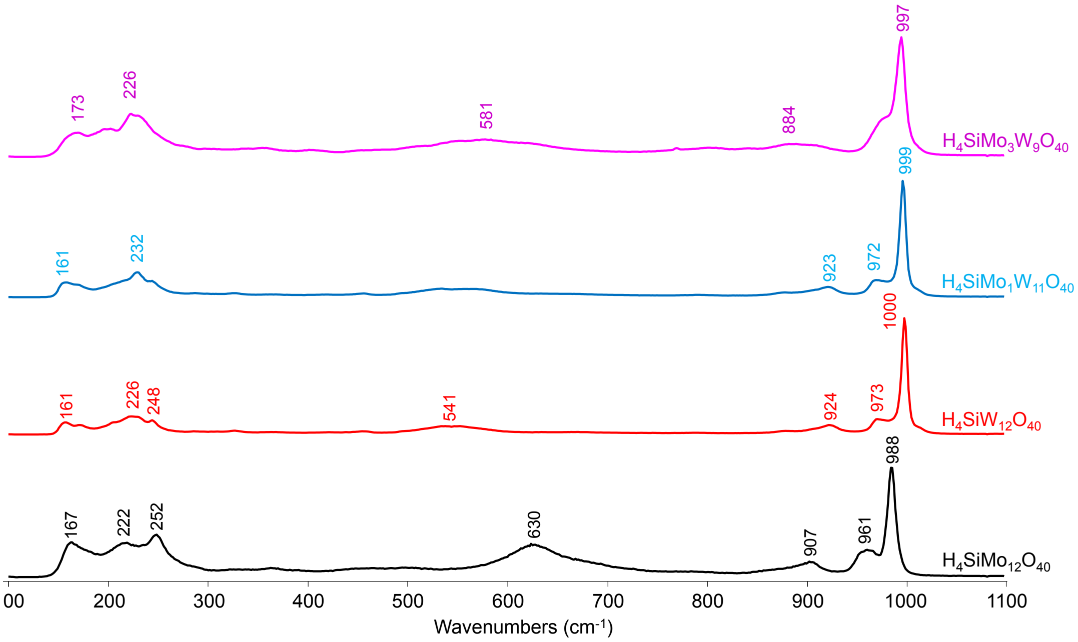

Figure 3. Raman spectra of bulk HPA: comparison of mixed HPA with the monometallic ones

Fig. 3 presents Raman spectra of $H_4[SiMo_1W_{11}O_{40}]$ and $H_4[SiMo_3W_9O_{40}]$. For comparison purposes, $H_4[SiMo_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ spectra have also been added on this figure. The mixed heteropolyacids present very close Raman spectra (as already observed for IR analysis) that are dominated by a main peak corresponding to a $M{=}O_t$ terminal vibration at the same wavenumber (about 997 cm^{-1}). This value is very similar to that of the $W{=}O_t$ vibration observed in the $H_4[SiW_{12}O_{40}]$ spectrum. The relative simplicity of the mixed MoW HPA Raman spectra shows that these spectra do not correspond to a mixture of both $H_4[SiMo_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ monometallic spectra. For mixed $SiMo_1W_{11}O_{40}^{4-}$ and $SiMo_3W_9O_{40}^{4-}$, due to similarity between Mo and W, $Mo{=}O_t$ and $W{=}O_t$ cannot be distinguished and the redistribution of potential energy in the mixed anion leads to the complete mixing of $W{=}O_t$ and $Mo{=}O_t$ vibrators.

DTA-TGA analysis

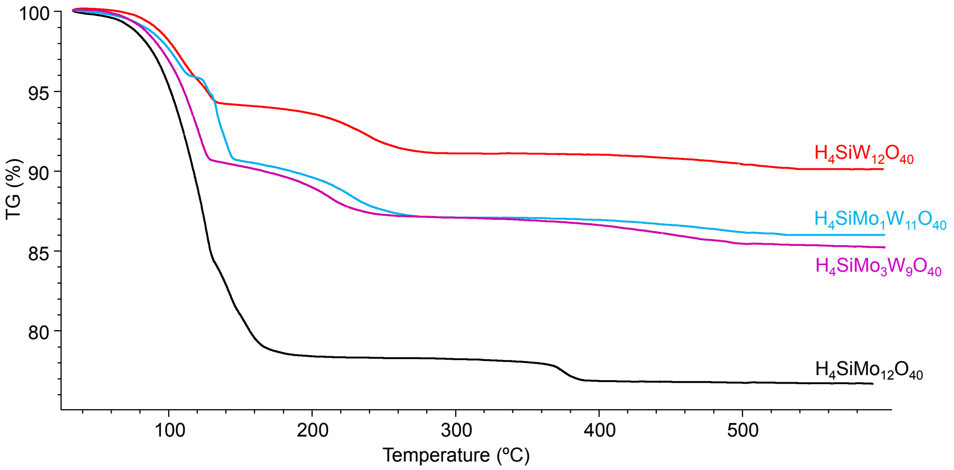

Figure 4. TGA curves of mixed and monometallic HPA

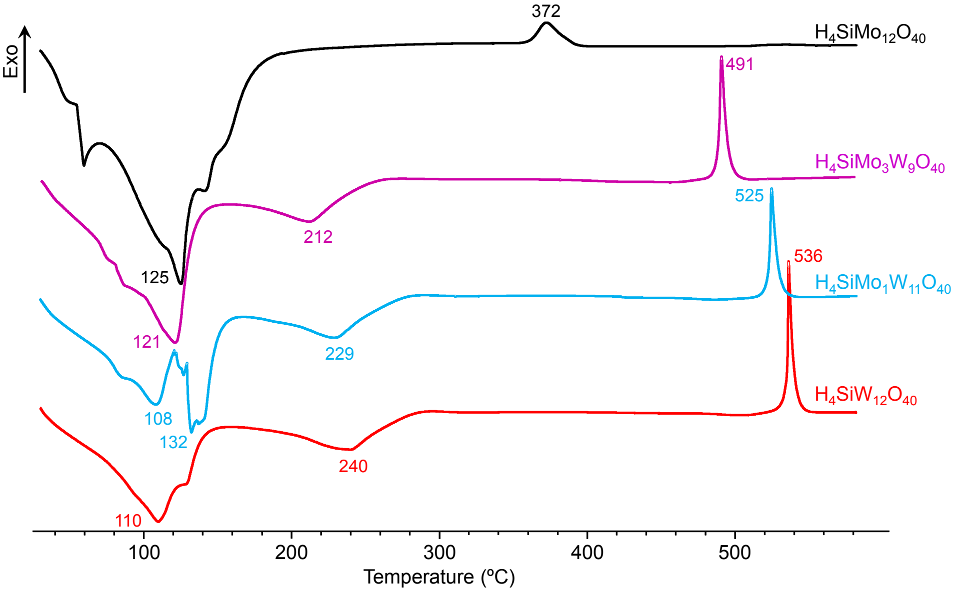

Figure 5. DSC curves of mixed and monometallic HPA

Thermal stability of mixed and monometallic HPA was evaluated by thermogravimetric analysis (TGA) and respective DSC analyses were also carried out. TG curves are reported Fig. 4 showing that the thermal behavior of the mixed HPA and silicotungstic acid is very similar and differs slightly from that of silicomolybdic acid. For this later well-known acid, an important first loss (23%) until 180°C, also characterized by an important endothermic peak in DSC (Fig. 5), corresponds to the release of 29 crystalline water molecules. After 180°C, a plateau is reached indicating the formation of the stable dehydrated $H_4SiMo_{12}O_{40}$ until 360°C. The second weight loss of 1.6 % is attributed to the loss of constituting water molecules giving rise to separate MoO_3 oxide and non-crystalline SiO_2. The exothermic peak in the DSC curve indicates a crystallization temperature around 370°C for MoO_3.

For silicotungstic acid and mixed HPA, the first weight loss observed between 25 and 180°C in $H_4SiMo_{12}O_{40}$ spreads out especially as the amount of tungsten increases reaching 260°C for silicotungstic acid. Moreover the important departure of crystalline water, also indicated by the endothermic peaks, occurs in two steps indicating the formation of a stable intermediate hydrate as $H_4SiW_{12}O_{40}$, 6 H_2O around 120°C in agreement with the weight loss of 6.7% before the formation of the dehydrated compounds corresponding to the plateau in the TG curves. The loss of constitutive water leading to the oxides formation is observed until the WO_3 crystallization represented by the exothermic peaks in DSC curves at 536, 525 and 491°C for $H_4SiW_{12}O_{40}$, $H_4SiMoW_{11}O_{40}$ and $H_4SiMo_3W_9O_{40}$ respectively, the substitution of W by Mo slightly decreasing the thermal stability of the mixed HPA compared to that of silicotungstic acid.

[1] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*,1983, **22**, 207-216.

[2] C. Rocchiccioli-Deltcheff, R. Thouvenot, R.Franck, *Spectrochim. Acta,* 1976, **A32**, 587-597.