Theoretical Study on the Substitution of Tungsten by Vanadium on Keggin Structures [XW$_{12-n}$V$_n$O$_{40}$]$^{-(q+n)}$ X=Si, P; 0<n<4.

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INTRODUCTION

Heteropolyanions (HPAs) are molecular structures resembling oxide fragments with well defined shape and size[1]. Among HPAs, Keggin structures, with [XM$_{12}$O$_{40}$]$^{q-}$ general formula, figure as the most relevant specie, counting for 2/3 of the published material about this compounds family, in which about 80% are on catalysis purpose[2]. Substitution of the heteroatom or of the metal (X, or M, respectively) give rise to different relations of acidity, reducing character and stability, tuning its conversion and selectivity on its catalytic activity. The preset work aim to analyze and compare a series of theoretical and experimental data to collaborate to the comprehension of the isomer formation mechanisms on the series [XW$_{12-n}$V$_n$O$_{40}$]$^{-(q+n)}$, with X=Si, P and 0≤n≤4, as well as to better interpretation of the vibrational spectra of infrared (IR) and Raman.

METHODS

The geometry optimization and vibrational frequency calculations were performed on DFT/B3LYP and M062X levels. The 6-31G* base set was used on phosphorus and silicon, wile 6-31+G* was used on oxygen, and the LanL2DZ effective core potential with relativistic effects implicitly included base set was used on vanadium and tungsten. The polarizable continuum model (PCM) with the integral equation formalism variant (Integral Formalism Polarizable Continuum Model – IEFPCM) was used on the calculations to count for charge stabilization effects due to the aqueous solvent on the studied anions.

RESULTS AND DISCUSSION

There are 47 different possible structures with 0 to 4 M substituents[4]. A good agreement between calculated geometry and experimental data was reached on the cases where the comparison is valid[5]. Gibbs free energy analyses shows small energy variation among species with same number of substituents, suggesting a thermodynamic factor leading to a observable amounts of different isomers among a given sample. Optimal relative ratio of isomers was shown to be sensitive on the heteroatom choice. Samples with different isomer distribution are expected to generate different IR spectra patterns. The coexistence of species with different number of substituents was shown to be thermodynamically unfavorable on the performed calculations; experimental observation of this coexistence most lie on kinetics factors. Experimental Raman spectrum didn't show characteristic V-O$_d$ bands present on the calculations and need to be further investigated.

CONCLUSIONS

It is thermodynamically expected to observe a isomer distribution on a given sample. Homogeneous distribution of the substituents is energetically favorable. IR bands can be used to differ between different isomer distributions and to identify substitution rate. Predicted characteristics Raman bands are not experimentally observed and need further investigations.

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