

ELECTRONIC SUPPORTING INFORMATION

Keggin-type Silicotungstates as efficient catalysts for sustainable oxidations with H₂O₂

Saete S. Balula^a *, Luís Cunha-Silva^a, Isabel C. M. S. Santos^b, Ana C. Estrada^c,
A.C. Fernandes^d, José A. S. Cavaleiro^b, João Pires^d, Cristina Freire^a, Ana M. V. Cavaleiro^b

^a *REQUIMTE & Departamento de Química e Bioquímica, Faculdade de Ciências,*

Universidade do Porto, 4169-007 Porto, Portugal;

^b *Departamento de Química, QOPNA, Universidade de Aveiro, 3810-193 Aveiro, Portugal;*

^c *Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal;*

^d *Departamento de Química e Bioquímica, CQB, Faculdade de Ciências, Universidade de Lisboa,*

Campo Grande C8, 1749-016 Lisboa, Portugal

*Corresponding author: Dr. Saete S. Balula; e-mail: sbalula@fc.up.pt; Tel.: +351 220402576; Fax: +351
220402659

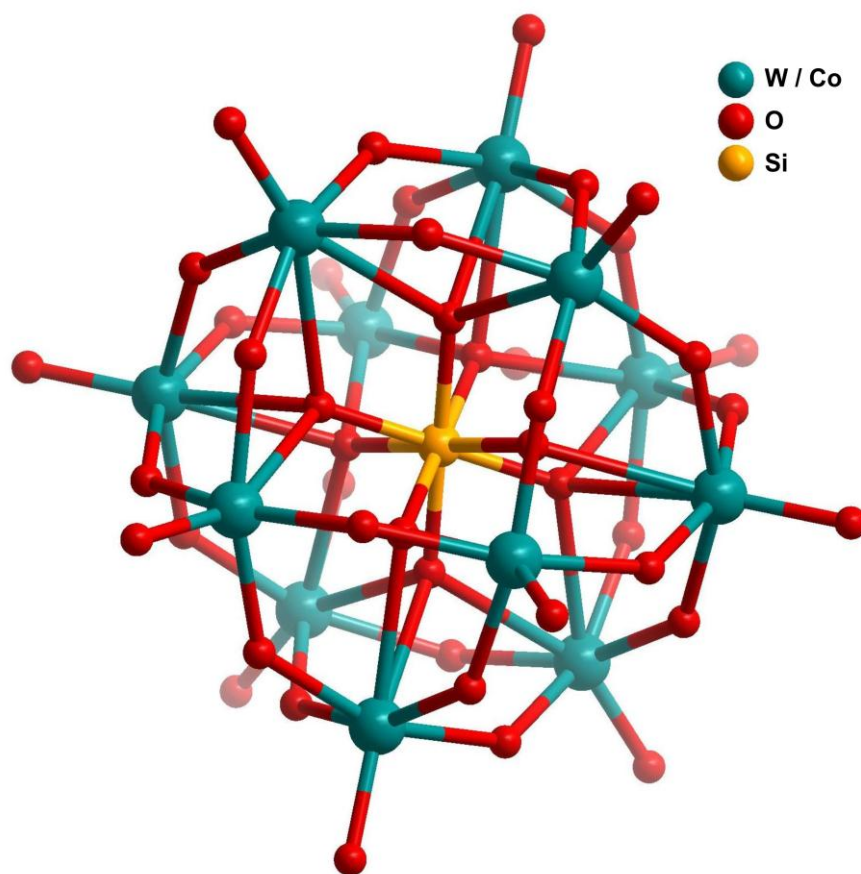


Figure S1. Ball-and-Stick representation of the polyoxoanion $[\text{SiW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}]^{6-}$ present in the compound $\text{K}_4\text{H}_2[\text{SiW}_{11}\text{CoH}_2\text{O}_{40}] \cdot 22\text{H}_2\text{O}$, $\text{KSiW}_{11}\text{Co}$.

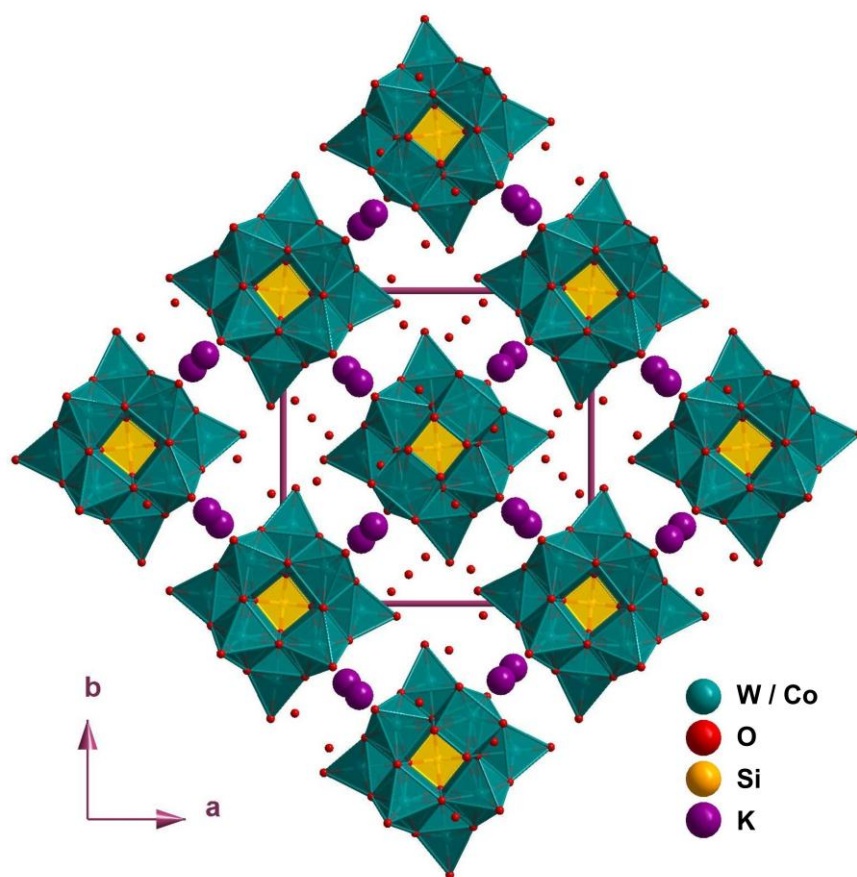


Figure S2. Crystalline packing of compound $\text{K}_4\text{H}_2[\text{SiW}_{11}\text{CoH}_2\text{O}_{40}] \cdot 22\text{H}_2\text{O}$, ($\text{KSiW}_{11}\text{Co}$) viewed along the $[001]$ direction of the unit cell.

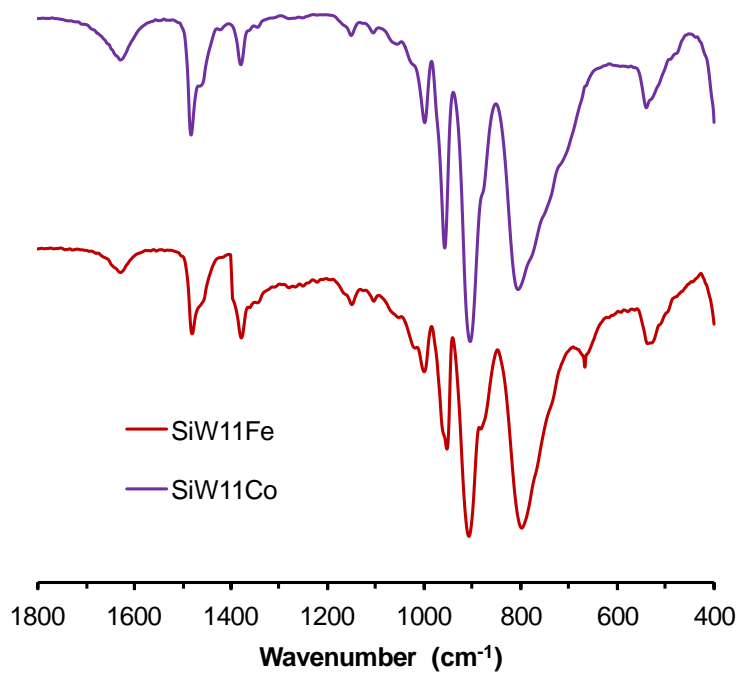


Figure S3. FT-IR spectra of the TBA salts of mono-substituted silicotungstates.

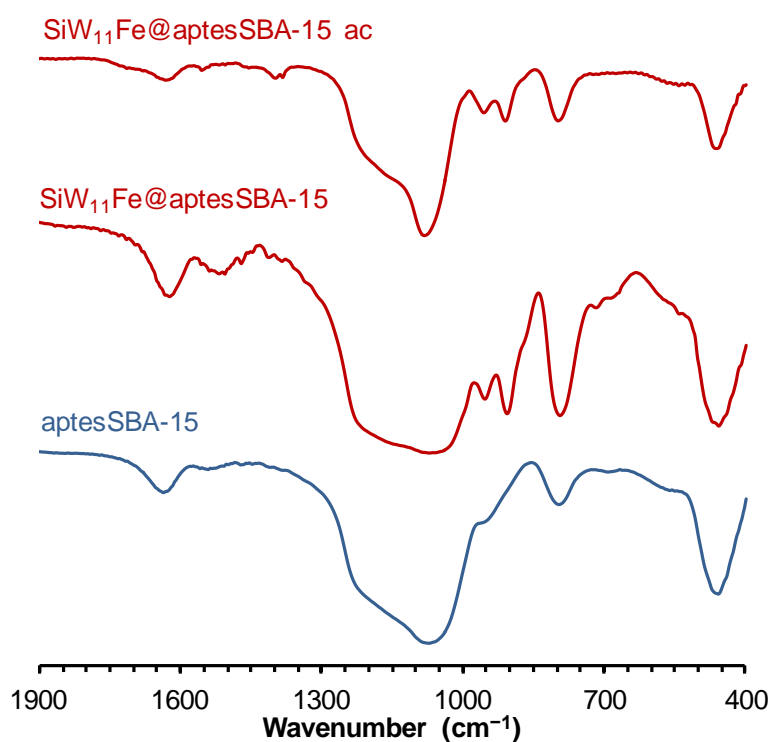


Figure S4. FT-IR spectra of support aptesSBA-15 and SiW₁₁Fe@aptSBA-15 composites before and after catalytic use in the wavenumber region between 400 and 1900 cm⁻¹. Name of sample with ac corresponds to recovered sample after catalyze the styrene oxidation reaction.

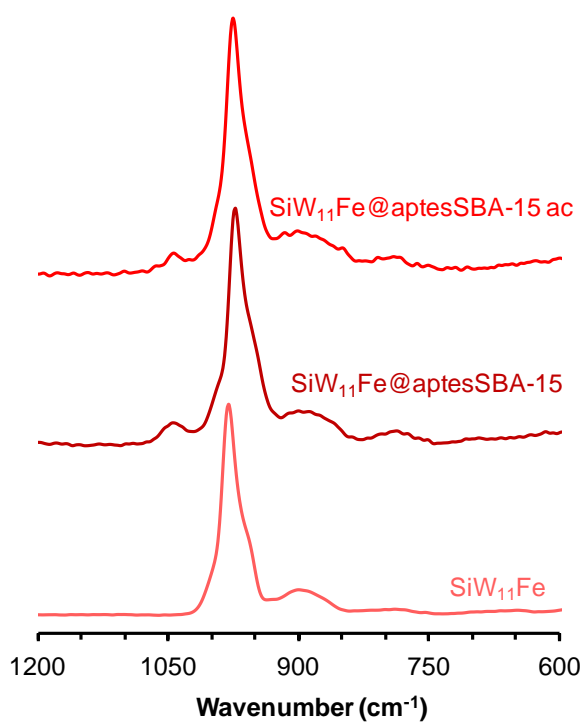
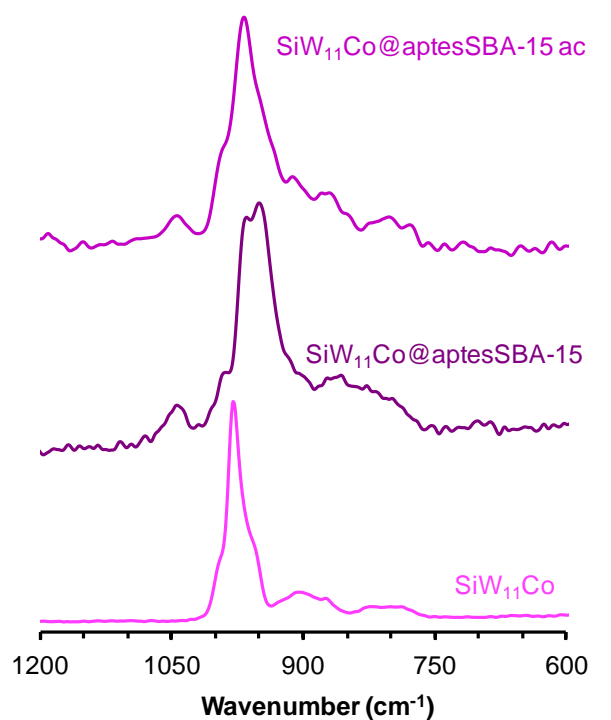


Figure S5. FT-Raman spectra of the TBA salt of silicotungstates and their composites before and after catalytic use in the wavenumber region between 600 and 1200 cm^{-1} . Name of samples with ac corresponds to recovered samples after catalyze the styrene oxidation reaction.

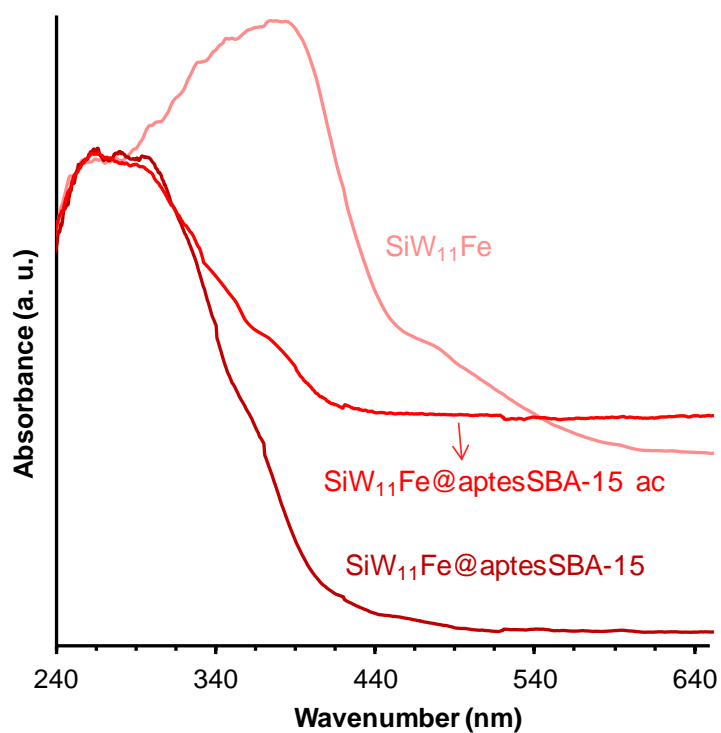


Figure S6. Diffuse reflectance spectra of mono-substituted SiW₁₁Fe and its composite before and after catalytic use (ac) in the wavenumber region between 640 and 240 nm⁻¹. Name of sample with ac corresponds to recovered sample after catalyze the styrene oxidation reaction.

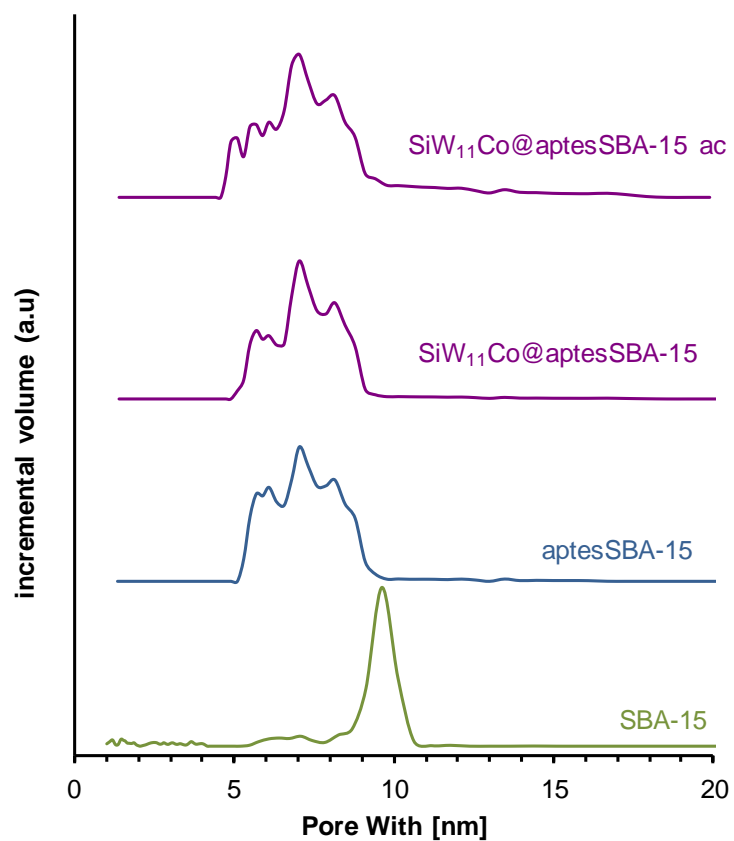


Figure S7. Nitrogen adsorption-desorption isotherms at -196 °C for the initial and modified SBA-15 samples. Name of sample with ac corresponds to recovered sample after catalyze the styrene oxidation reaction.

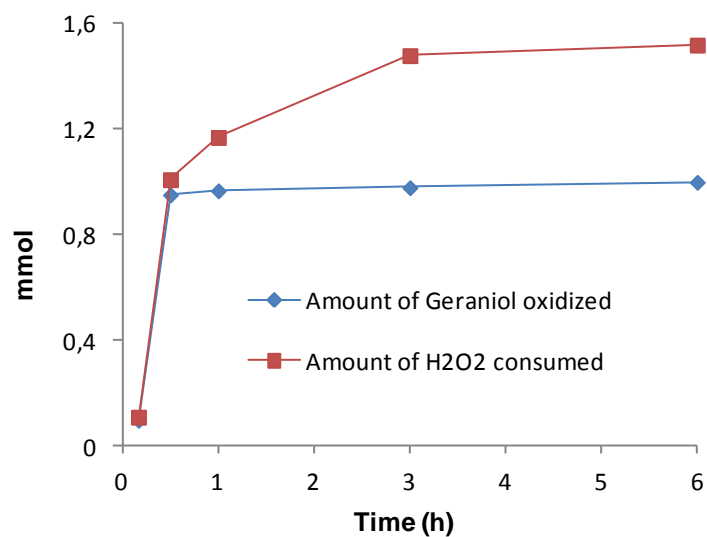


Figure S8. Comparison between the amount of geraniol oxidized and the amount of oxidant H₂O₂ consumed in the reaction catalyzed by the homogeneous SiW₁₁Co and using acetonitrile as solvent.

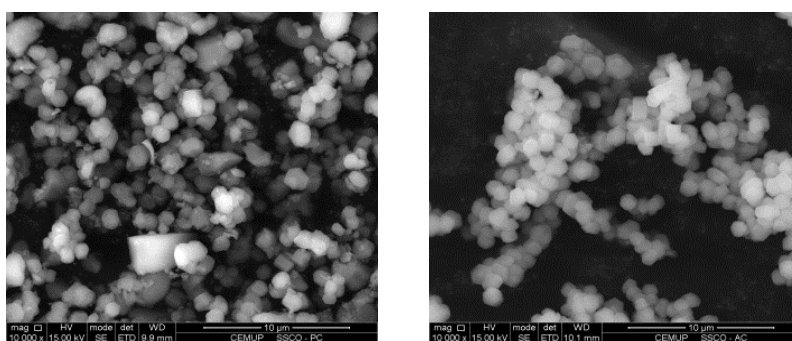


Figure S9. Scanning Electronic Microscopy images of SiW₁₁Co@aptesSBA-15 before (left) and after (right) to be used as catalyst in the oxidation of styrene with H₂O₂.