Synthesis, characterization and applications of Polyoxometalate-based Ionic Liquids

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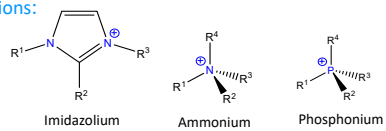
In the context of sustainable chemistry, Ionic Liquids (ILs) were among the first "green" solvents used. A wide variety of ILs exists, including polyoxometalate(POM)-based ILs[1] usually used as catalysts in desulfurization of fuels[2] and oxidation reactions[3] or in depollution[4]. Herein, synthesis and characterization of a new POM-based ILs and its application in oxidation catalysis of organic molecules are presented.

Ionic Liquids (ILs) mp < 100°C

- High stability (thermal and chemical)
- Low vapor pressure (at r. t.)
- High conductivity
- Recyclability

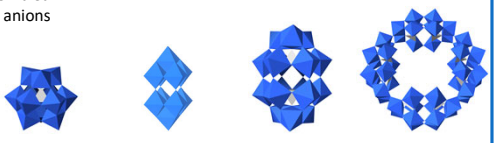
Cations:



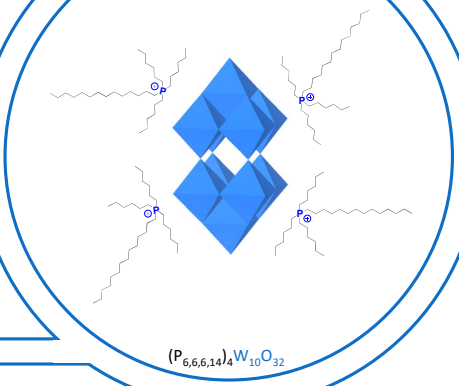
Anions: Organic MsO^-, TsO^-, $CH_3CO_2^-$ ... Inorganic Cl^-, Br^-, BF_4^-, PF_6^-, ClO_4^- ...

Polyoxometalates (POMs)

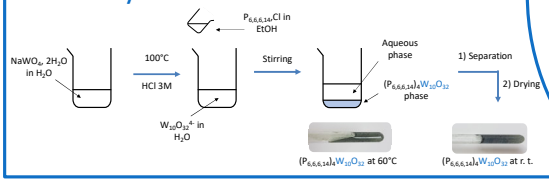
- Soluble polynuclear anionic metal oxide
- Composed of metals in their highest oxidation state (W or Mo)
- MO_6 octahedra assembled around template anions



POM-IL

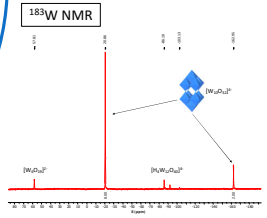


POM-IL synthesis

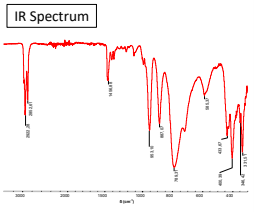


Characterizations

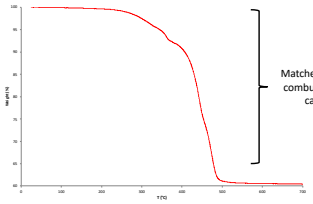
^{183}W NMR



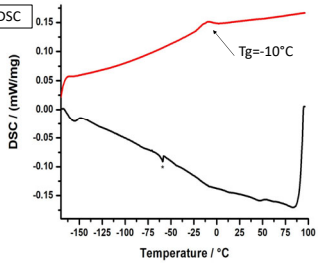
IR Spectrum



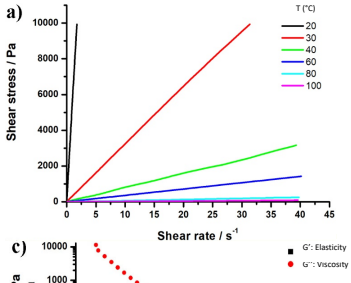
TGA

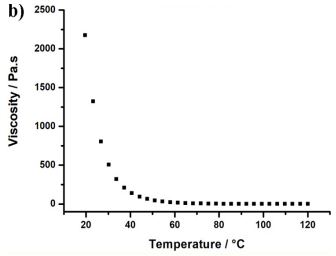


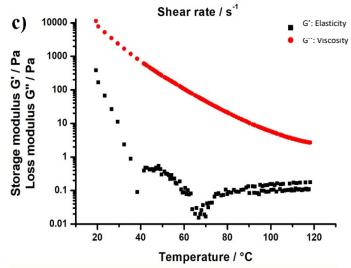
DSC

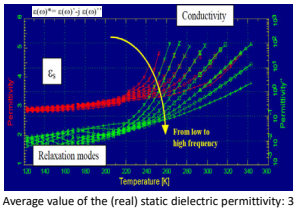


Rheological measurements







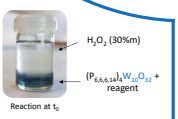


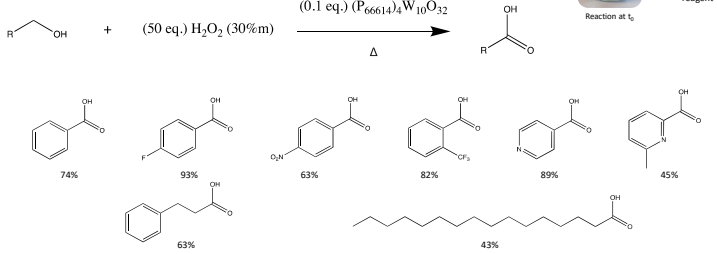
Average value of the (real) static dielectric permittivity: 3

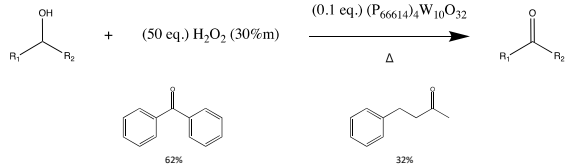
All of these analyses confirm the formation of $(P_{6,6,6,14})_4W_{10}O_{32}$ and its good solvent and ionic liquid properties

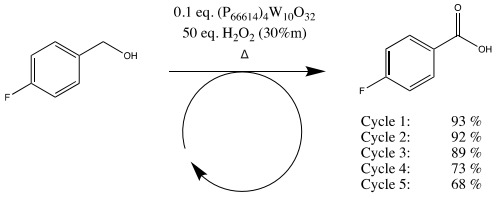
Alcohols oxidation

Biphasic reaction between (POM-IL + reagent) and H_2O_2-H_2O









Cycle 1:	93 %
Cycle 2:	92 %
Cycle 3:	89 %
Cycle 4:	73 %
Cycle 5:	68 %

In conclusion, the accurate choice of cations coupled with POMs allows the creation of ionic liquids. The features of the resulting POM-IL are improved thanks to the oxidative property of the POM and solvent nature of the IL.

Perspectives:
- Oxidation of other organic molecules
- Scope of POM-IL
- Reaction mechanism study
- UV-Visible oxidation reaction

References:
[1] Nancy Watfa, Sébastien Floquet et al., Soft Matter, **2015**, *11*, 1087-1099
[2] Benjamin Bertleff, Jakob Albert et al., ACS Sustainable Chem. Eng., **2017**, *5*, 4110-4118
[3] Li Jing, Weidong Zhu et al., Ind. Eng. Chem. Res. **2013**, *52*, 10095-10104
[4] Sven Herrmann, Carsten Streb et al., Angew. Chem. Int. Ed., **2017**, *56*, 1-5