

# Keggin heteropolyanions: novel versatile deoxydehydration catalysts

<u>Alixandre MAGERAT</u><sup>\*</sup>, Sophie HERMANS, Eric M. GAIGNEAUX Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Place Louis Pasteur, 1 – 1438 Louvain-la-Neuve, Belgium \*alixandre.magerat@uclouvain.be

### Significance and Relevance

Deoxydehydration (DODH) is an important reaction to upgrade (bio-based) polyols and make them practically useful<sup>1</sup>. Catalysts for this transformation are generally Mo, Re or V-based organometallics or oxides<sup>2</sup>, while the use of Keggin heteropolyanions (HPAs) has never been reported before. We report here, for the first time, the promising catalytic performance of  $(TBA)_3PMo_{12}O_{40}$  (TBA = tetrabutylammonium), a simple HPA obtained by precipitation of the commercially available  $H_3PMo_{12}O_{40}$  with TBA<sup>+</sup>. Additionally, we show that substituting a W by Re in  $PW_{12}O_{40}^{3-}$  dramatically increases its DODH-activity, hence demonstrating the high versatility of HPAs. Characterizations (IR, <sup>31</sup>P NMR and UV-vis) of the used catalysts are provided to investigate the nature of the active species of these novel catalysts.

Preferred and 2<sup>nd</sup> choice for the topic: "Green Chemistry and biomass transformation, renewable resources conversion"

Preferred presentation: Oral only

## **Introduction and Motivations**

Most of today's chemicals production relies on fossil fuels, but their finite nature requires exploring alternative raw material sources. The use of biomass-derived compounds as such is a promising yet challenging option due to their polyoxygenated nature, often under the form of polyhydroxylated chains. Such functionality (vicinal diols) can be transformed into readily functionalizable alkene through DODH (Fig. 1). Hereunder, we describe a pioneering work where Keggin HPAs are used as DODH catalysts for the very first time.



Figure 1. Deoxydehydration reaction. The number of  $H_2O$  molecules produced depends on the reductant's nature.

## **Results and Discussion**

Keggin phosphomolybdates and -tungstates  $(PM_{12}O_{40}^{3^{-}} = PM$  with M being Mo or W) were first considered as potential catalysts and tested in the model DODH of 1,2-hexanediol into 1-hexene (reaction on Fig. 2 (b)). Three different counter-cations were considered, namely H<sup>+</sup> (HPM), NH<sub>4</sub><sup>+</sup> (NH<sub>4</sub>PM) and tetrabutylammonium (TBAPM) (Fig. 2 (a)). Within both W and Mo series, TBAPMs showed the highest 1-hexene yields. This was attributed to the absence of Bronsted acidity as the latter is known to be undesired for DODH catalysis, hence explaining the lower yields obtained with HPMs and NH<sub>4</sub>PMs.

Additionally, PW demonstrated lower-DODH activity than their PMo counterparts, likely because W has less redox flexibility than Mo. To improve the DODH activity of TBAPW, we consented to a synthetic effort to replace one of the 12 tungsten atoms in the PW anion by a rhenium(V) one, yielding  $(TBA)_4PW_{11}Re^{V}O_{40}$  (TBAPW<sub>11</sub>Re). The latter was fully characterized by <sup>31</sup>P NMR, IR (Fig. 2 (d-f)), ICP-AES,



PXRD and UV-vis (not shown here). The obtained 1-hexene yield was greatly improved with TBAPW<sub>11</sub>Re, increasing from 9% for TBAPW to 73% for TBAPW<sub>11</sub>Re (Fig. 2 (b)).

Recyclability tests (Fig. 3 (c)), combined with IR and <sup>31</sup>P NMR analyses (Fig. 3 (d-f)), revealed that TBAPMo and TBAPW<sub>11</sub>Re undergo partial, non-destructive dissolution during catalytic tests. Indeed, TBAPW<sub>11</sub>Re showed the same IR and <sup>31</sup>P NMR spectrum before and after catalysis.



**Figure 2**. Catalytic performances of (a) HPMs, NH<sub>4</sub>PMs and TBAPMs (M=Mo or W) at different temperatures and (b) TBAPMo, TBAPW, TBAHPW<sub>11</sub> (monolacunary form of TBAPW, (TBA)<sub>4</sub>H<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>) and TBAPW<sub>11</sub>Re at 210°C. Reaction conditions: 18h; 5 mL of 1,2-hexanediol (0.1 mol/L) with n-dodecane as internal standard (0.1 mol/L); 5% Mo or W mol. or 2% mol Re. (c) Recycling experiments with TBAPMo and TBAPW<sub>11</sub>Re. (d) IR and <sup>31</sup>P NMR (e-f) spectra of TBAPMo and TBAPW<sub>11</sub>Re before and after catalytic tests.

After catalysis, TBAPMo presented several peaks in <sup>31</sup>P NMR that are attributed to several (TBA)<sub>3</sub>PMo<sup>VI</sup><sub>12-x</sub>Mo<sup>V</sup><sub>x</sub><sup>x-</sup> species. The one-electron reduced TBAPMo could be obtained when it was reacted with Br<sub>2</sub>, showing the reversibility of this reduced state. TBAPMo after catalytic test presented the same IR spectrum as before, at the exception of broadened Mo-O-Mo bands with decreased intensity. This behaviour has already been reported and is due to a strong coupling of bipolaron with the vibration of the bridging Mo-O-Mo bonds<sup>3</sup>. Hence, these results are also in line with a preserved Keggin structure.

## Conclusion

This work represents the pioneering use of Keggin polyoxometalates as a versatile platform for the elaboration of performant deoxydehydration catalysts and is laying the groundwork for future catalytic systems including Keggin POMs for biomass valorization processes. Future works will entail exploring new POM formulations and optimizing their recovery and reuse.

## Acknowledgements

The Université catholique de Louvain (UCLouvain) is acknowledged for the teaching assistant position.

## References

- 1. F.C. Jentoft, Catal. Sci. Technol. 2022, 12, 6308-6358.
- 2. N.N. Tshibalonza, J.C.M. Monbaliu, Green Chem. 2017, 19, 3006-3013.
- 3. M. Fournier, C. Rocchiccioli-Deltcheff, L.P. Kazansky, Chem. Phys. Lett. 1994, 4, 297-300.