Induction of catalytic reactivity by self-organization of a binuclear Cr complex in the ionic liquid mediated dehydration of glucose

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**Introduction**

- HMF is considered a key biobased platform molecule
- Catalytic dehydration of fructose gives HMF in high yields
- Selective glucose dehydration is a challenge

**State of Cr in the ionic liquid medium**

**Glucose dehydration by CrCl2 in EMImCl**

**Reaction mechanism**

**Initial coordination of glucose**

**Summary**

- Transient formation of Cr dimers induces glucose conversion
- Self-organization of the reaction environment
- Non-innocent solvent: crucial role of basic anions of IL, while the organic cation is not affecting reactivity

"Nature mimics Nature" at the difficult step active site resembles enzymatic

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**Fig. 1** Sugar conversion and HMF yield from fructose (left) and glucose (right) in EMImCl ionic liquid in the presence of metal chloride catalysts.

- CrCl2/EMImCl system is uniquely active and selective.1

**Fig. 2** DFT-computed relative stabilities of potential Cr chloride complexes in a model MMImCl ionic liquid.

**Fig. 3** A comparison of XRD data for a CrCl2/EMImCl co-crystal,2 the results of liquid phase XAS and DFT calculations.3

**Fig. 4** DFT and EXAFS data on glucose complexation with CrII centers

- Only mononuclear 4-coordinated CrII complexes are formed prior to the catalytic transformations of glucose
- Reversible coordination is necessary to establish a coordination via O1 from which subsequent transformations can occur.

**Fig. 5**

In situ EXAFS: transient formation of binuclear Cr species

DFT: Self-organization of Cr ions into a binuclear complex at the rate-limiting step.

All other reaction steps are catalyzed by mononuclear CrII complexes.

Generic mechanism: does not depend on the oxidation state and the type of the cation.6

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