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Reversible Electrocatalysis by Enzymes of Relevance to Renewable Energy Conversions

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Renewable energy needs excellent electrocatalysts, based upon inexpensive scalable technology, for splitting water and activating CO₂ to produce fuels as well as converting fuels and oxygen into electricity [1]. The most efficient electrocatalysts operate 'reversibly', i.e. they catalyse an electrode reaction in either direction without a significant overpotential being required [2-4]. An outcome of recent research has been the realisation that many redox enzymes, despite being giant, unstable molecules for which most of the bulk interior is electronically insulating, come very close to exhibiting this very special characteristic yet contain abundant elements in place of platinum metals. An important aim to establish the precise features of an active site that make it so effective in electrocatalysis – predicting what part of the greater mass of surrounding material could be 'trimmed off'. Active sites of enzymes have all the right groups positioned in all the right places, a factor that is absent from small metal complexes or surfaces unless the appropriate second and outer coordination shells are built into the structure.

Protein film electrochemistry has proved to be a valuable tool for studying redox enzymes, along with genetic engineering, spectroscopy and crystallography. This lecture will summarise a few of the most interesting and significant lessons learnt so far, and address some new observations that are relevant for understanding enzyme mechanism and transferring the knowledge into the design of catalysts for renewable energy conversions.

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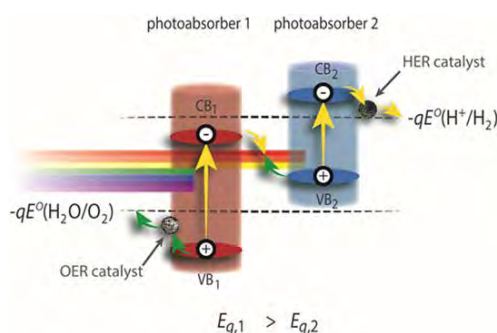
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Earth-abundant Electrocatalysts for Solar Fuels Production

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The efficient and inexpensive production of chemicals using sunlight is a promising alternative for the sustainable generation of carbon-free fuels and the storage of solar energy. Sunlight can be harvested in artificial photosynthetic systems as the one shown in Figure 1 to split water and produce hydrogen fuel. Such dual-absorber tandem photoelectrochemical (PEC) systems have been predicted to reach over 25% solar-to-hydrogen conversion (STH) efficiencies when realistic energy losses are taken into account[1]. To date, various artificial photosynthetic systems have been proposed, and monolithic devices with STH efficiency of up to 18% have been experimentally demonstrated [2]. However, these high efficiency devices employ expensive photoabsorbers and noble metal electrocatalysts, which are prohibitive for large scale application. In this contribution, highlights of our comprehensive approach towards the development of inexpensive devices for unassisted water splitting are presented.



In particular, the coupling of molybdenum carbide and amorphous molybdenum sulfide as hydrogen evolution reaction (HER) catalysts to surface-protected photocathodes is discussed [3-5]. The development of the first photocathodes for PEC hydrogen production in alkaline solutions, where photoanodes for the complementary oxygen evolution reaction (OER) have been extensively developed is presented and the importance of working in harsh alkaline conditions is discussed [4,5]. Similarly, the development of a general and simple method for the deposition of optically transparent OER catalyst on hematite photoanodes is described [6]. The developed hematite photoanode is coupled to a perovskite cell to create a tandem cell device capable of unassisted water splitting with high solar-to-hydrogen efficiencies of ~2% with long term stability. This is one of the first devices made entirely of Earth-abundant elements for the efficient production of solar fuels.

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[6] Carlos G. Morales-Guio, Matthew T. Mayer, Aswani Yella, S. David Tilley, Michael Grätzel, Xile Hu, *Submitted*

Halogen chemistry on rutile-type catalysts

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A set of complementary advanced methods including Density Functional Theory (DFT), Temporal Analysis of Products (TAP), and Prompt-Gamma Activation Analysis (PGAA) has been applied to assess mechanistic analogies between HBr and HCl oxidation on rutile-type catalysts. This provided an in-depth picture of the halogen chemistry on these materials, ranging from the atomic level understanding of the reaction pathway to the insitu determination of halogen coverages during hydrogen halide oxidation at ambient pressure. We experimentally verified that halogen evolution determines the catalytic activity as postulated by theory.¹ Additionally, we found that the self-doping mechanism of HBr oxidation over TiO₂ leads to a moderate bromine coverage (50%) in sharp contrast to RuO₂ which undergoes subsurface bromination.

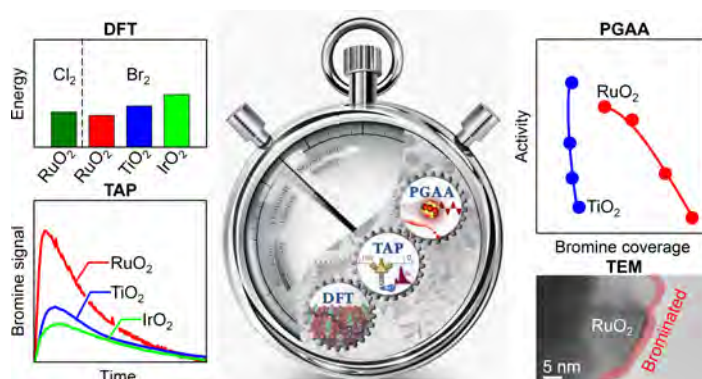


Figure 1. Like cogwheels in a watch. The integration of different techniques enables a synchronized analysis of the halogen chemistry on rutile-type catalysts from the atomic to macroscopic level.

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Intermediates in the Photochemical Dehydrogenation of Borane-Amines

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Key words: Metal carbonyl, dehydrogenation, hydrogen storage, ammonia borane, dehydrocoupling, time resolve IR spectroscopy, fuels, fuel cell

Due to high volumetric and gravimetric hydrogen content, Boranes-Amine ($\text{H}_3\text{BNH}_n\text{R}_{3-n}$; R=H, alkyl, aryl) have been extensively explored as portable hydrogen source and storage materials. In this context, B-H bond activation by transition metals is an area of active research as it provides an appealing method to release hydrogen from amine-boranes (dehydrogenation) at moderate temperatures and reasonable rates. Photolysis of $\text{CpM}(\text{CO})_3$ (M=Mn, Re, and Fe) in the presence of H_3BNEt_3 yields M-H-B intermediates and Cis/trans- $\text{CpRe}(\text{CO})_2(\text{H})_2$ complex (Figure 1). This finding presents a rare example of transition metal mediated dehydrogenation of a tertiary amine-borane and suggests that the abstracted hydrogens may be stored in the form of metal hydride complexes.¹ New findings in the photochemical activation of amines-borane by Iron-hydrogenase would also be presented.

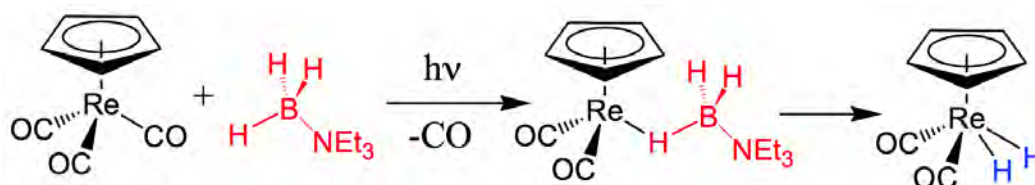


Figure 1: Photochemical pathway of metal carbonyl complexes under UV irradiation in solution

Aknoledge: We thanks Qatar Foundation for the funding.

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Challenges in photocatalytic water reduction with nickel containing polyoxometalates

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Complete systems for artificial photosynthesis as an elegant way to clean solar fuels require the combination of water reduction catalysts (WRCs) and water oxidation catalysts (WOCs).^[1-3] Due to their rich redox and structural chemistry, polyoxometalates (POMs) as highly negatively charged oxoclusters have been widely investigated for their water oxidation catalyst activity, while their use as WRCs is just about to be explored. Many of the previously reported POM based WRCs require the presence of a noble metal co-catalyst, such as platinum,^[2] and clear structure-activity relationships for their design remain to be established.

It has been shown that the redox properties of small Keggin-type POMs can be tuned by variation of the central hetero-element X.^[4] Based on these electrochemical trends, we studied the influence of the hetero-element on the photocatalytic H₂ evolution using nickel-containing Keggin-POMs ([Ni(H₂O)XW₁₁O₃₉]ⁿ⁻; X = P, Si, Ge) as WRC prototypes.^[5] We discovered a clear dependence of the WRC activity on the hetero-atom, and the best performance was observed for X = Ge. Further electrochemical and DFT studies were conducted in search of SAR-based construction guidelines for POM-WRCs. Interestingly, the photo- and electrochemical pathways of the title compounds were found to differ considerably. Follow-up investigations on SAR of sandwich-type POMs are in progress.

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Development of MTPROP[®] catalysts: Basis for the realisation of the Methanol-To-Propylene process

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In consequence of declining mineral oil reserves, intensified by a rising standard of living in most parts of the world, the future demand of propylene (and its consecutive products, e.g. polypropylene) can no longer be covered on a base of mineral oil alone. The envisioned intensified exploitation of shale gas resources further aggravates this situation. This so-called “propylene gap” must be covered in future. Based on alternate raw materials such as natural gas, coal or biomass, the depleting raw material propylene is produced via methanol as intermediate. The highly selective “Methanol to Propylene” (MTP[®]) process [1] hosting Clariant’s MTPROP[®] catalyst [2] displays the heart of this approach. The presentation will outline the catalyst development from small-scale research laboratory samples towards a commercial catalyst scaling several hundred tons [2,3].

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Synthetic Chemistry to Reduce CO₂ EmissionsM. Kanan¹

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Synthesizing organic compounds using CO₂ and reducing equivalents provided by renewable energy could reduce greenhouse gas emissions by displacing fossil fuel use and incentivizing carbon capture. In order to be implemented on a significant scale, these processes must be cost-competitive with fossil fuels. The key technical challenge is to efficiently transform CO₂ into multi-carbon compounds because these targets generally have higher value, greater energy density, and more applications than C₁ compounds. An appealing strategy is to produce H₂ using H₂O splitting and then synthesize fuels and chemicals by hydrogenating CO₂. However, currently available CO₂ hydrogenation methods are only useful for synthesizing C₁ compounds such as methane, CO, and methanol. In this talk, I will describe a new CO₂ hydrogenation method that requires no transition metal catalysts and produces multi-carbon organic carboxylate products directly. Esterification and hydrogenation of the carboxylates provides energetically efficient, low carbon-footprint access to compounds including ethanol and ethylene glycol. Using a similar strategy, we have also developed a novel C-H carboxylation reaction that uses no transition metals. This reaction enables highly efficient syntheses of aromatic dicarboxylates for commodity polyester synthesis. Mechanistic insights and the steps required to scale these CO₂ hydrogenation and C-H carboxylation reactions will be discussed. This chemistry provides a foundation for transforming CO₂ from a greenhouse gas into a valuable synthetic feedstock.

Incorporation of ruthenium catalytic centers in phosphine-functionalized metal-organic frameworks

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The immobilization of transition metal catalysts in metal-organic frameworks (MOFs) has recently received much attention due to the chemical flexibility and porosity of this class of materials.[1] While supported nanoparticles offer high activity, they often lack the selectivity to compete against their homogeneous counterpart. Here we discuss our recent strategies to immobilize molecular ruthenium active sites within the pores of LSK-15, a MOF containing phosphine and amine functional groups.[2]

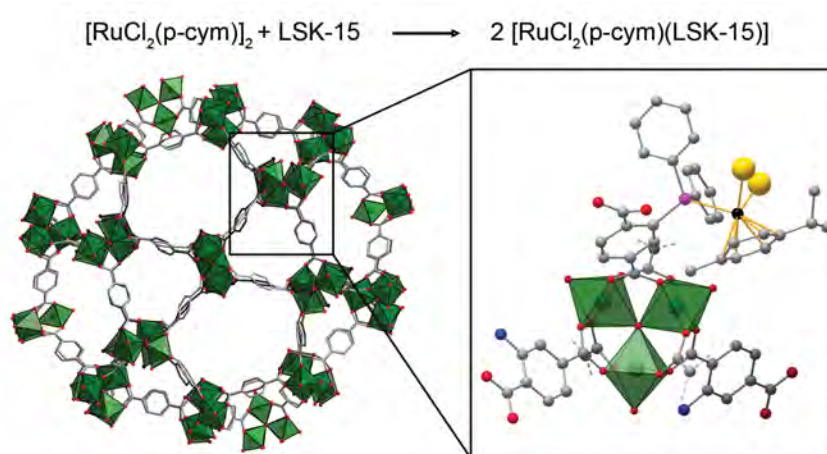


Figure 1. Schematic representation of LSK-15 with coordination details of a ruthenium active center at the phosphine site.

To illustrate the potential of phosphine MOFs in catalytic applications, a $[\text{Ru}(\text{Cl})_2(\text{p-cymene})]_2$ complex was immobilized in LSK-15 for the selective dehydrogenation of formic acid in the gas phase (Figure 1). The catalyst exhibited high catalytic activity ($\text{TOF} = 2400 \text{ h}^{-1}$) and selectivity towards hydrogen with outstanding stability ($\text{TON} > 470'000$ without sign of deactivation). The MOF scaffold maintained the fine dispersion of ruthenium centers, despite partial loss of the long-range order. A wide range of characterization, such as X-ray diffraction, ^{31}P and ^{13}C solid-state MAS NMR, electron microscopy and nitrogen physisorption were used to determine the stability of both active site and framework.

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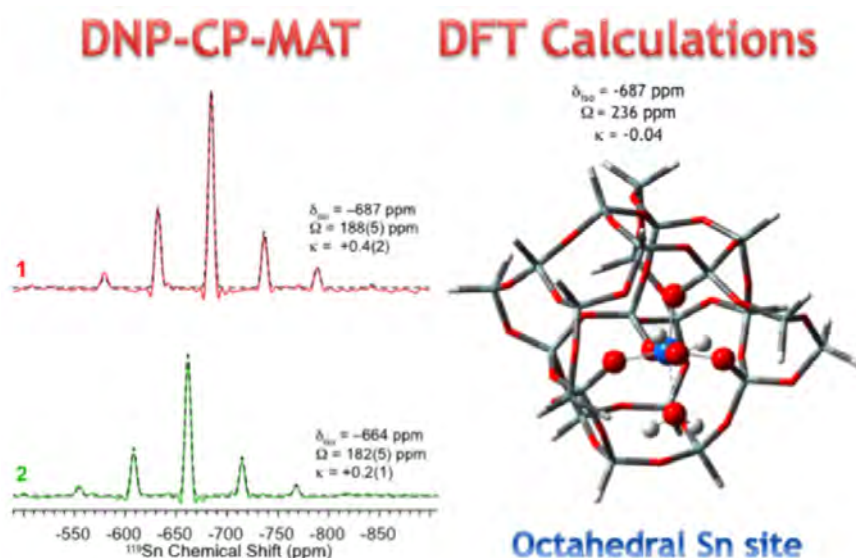
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NMR Signatures of the Active Sites in Sn- β Zeolite

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Characterizing the active sites in heterogeneous catalysts is a challenging endeavor and is key in order to establish structure-reactivity relationships. Single-site catalysts do not only facilitate the mechanistic analysis but they also show activity in a variety of chemical reactions. Sn- β , which consists of Sn^{IV}-sites embedded in the zeolite- β framework, is a prominent example of this type of catalysts. The uniform distribution of isolated Lewis acid sites, in combination with the unique hydrophobic pore architecture of the material, results in an unrivalled catalytic performance. The catalyst is active in the Bayer-Villiger oxidation of ketones, the isomerization and epimerization of sugars or the Meerwein-Ponndorf-Verley-Oppenaur reaction.[1-3] Despite intensive investigations, the structure of the active sites in Sn- β zeolites is not clear and remains a matter of intense debates. In the present contribution, we will present our work on the characterization of the active sites in the Sn- β zeolite both in dehydrated in hydrated forms.[4] By combining Dynamic Nuclear Polarization (DNP) NMR and DFT Calculations we unambiguously show the presence of framework Sn(IV) active sites in an octahedral environment in the hydrated form of the catalyst. The ¹¹⁹Sn NMR signal is found to be extremely sensitive to small chemical changes around the Sn center. We found that the signals of the active form of the catalyst probably correspond to the so-called open and closed sites, respectively (namely, tin bound to three to four siloxy groups of the zeolite framework).



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Active and spectator Ce^{3+} species in a ceria-based platinum catalyst during low-temperature CO oxidation

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Ceria, a material with high oxygen storage capacity, is often used as dopant and as support material for catalysts. Its ability to reversibly store and release oxygen can compensate for oxygen fluctuations in a gas supply and it can provide oxygen to catalytically active sites. Ceria-supported platinum nanoparticles show higher activity for low-temperature carbon monoxide oxidation than platinum nanoparticles on inert supports, such as alumina^[1]. The beneficial role of ceria is the activation of oxygen, which reacts with carbon monoxide at the platinum-ceria interface. Often the presence of Ce^{3+} is related to activity, however, direct spectroscopic evidence of the involvement of reduced ceria in a catalytic cycle is missing.

To probe the reactivity of ceria we monitored the rates of Ce^{3+} formation under transient conditions using in situ resonant X-ray emission spectroscopy (RXES). The formation of Ce^{3+} species was much slower than their re-oxidation (Figure 1 left). This indicates that active Ce^{3+} is short-lived under steady-state conditions. As the initial rates of Ce^{3+} formation, directly after oxygen supply was switched off, are very similar to the rates of steady-state carbon monoxide conversion (Figure 1 right), the Ce^{3+} formation is involved in the rate determining step of the catalytic cycle^[2]. In addition to this short-lived Ce^{3+} , we also observed inactive Ce^{3+} spectators (Figure 1 left). Our study shows spectroscopic evidence of the active role of Ce^{3+} in a catalytic cycle as well as non-active spectator Ce^{3+} . Overall, there is no relationship between the amount of observed Ce^{3+} under steady-state conditions and catalytic performance.

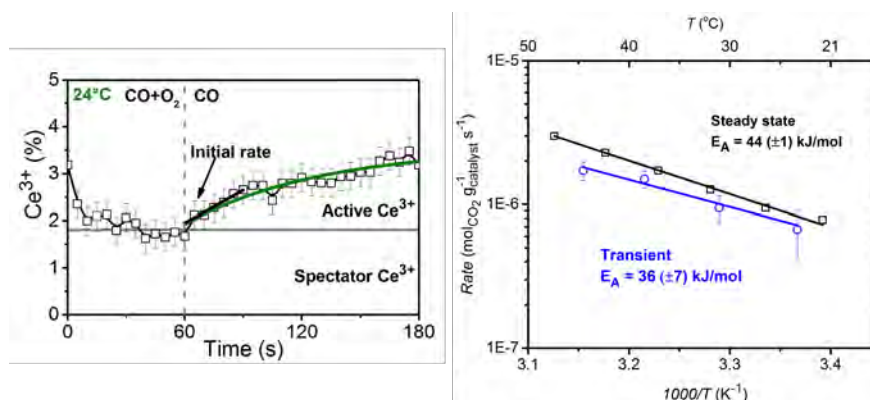


Figure 1: Left: Transient Ce^{3+} concentrations in the catalyst in 1% CO + 4% O₂ in He (0-60sec) and after the removal of O₂ from the gas atmosphere in 1%CO in He (60-180sec). **Right:** Arrhenius-type plot comparing the CO₂ formation rates calculated from the transient RXES measurements (blue circles) and the steady-state CO₂ formation rates obtained from gas chromatography (black squares).

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Generation of NH_3 -SCR active catalysts from decomposition of supported FeVO_4

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The selective catalytic reduction (SCR) of NO_x by NH_3 is up to date the world-wide most efficient post treatment method for reducing nitrogen oxides emissions from stationary and mobile sources. Recent studies show that various metal vanadates, such as FeVO_4 , ErVO_4 or TbVO_4 demonstrate promising NH_3 -SCR activity [1 - 3]. The high melting point of e.g. FeVO_4 (ca. 850°C) compared to V_2O_5 (ca. 690°C) makes them attractive for high temperature stable SCR catalysts [2]. Herein, we report the effect of catalyst loading, composition and calcination temperature on NH_3 -SCR activity was investigated of metal vanadates of the type $\text{Fe}_x\text{Al}_{1-x}\text{VO}_4$ ($0 \leq x \leq 1$) supported on TiO_2 - WO_3 - SiO_2 (TWS) [4].

The loading study (calcination temperature, 700°C / 10h) reveals that a low vanadate content is beneficial for the temperature stability of the catalyst, while a higher vanadate loading is advantageous for the activity in the low temperature regime. An increasing aluminum content was disadvantageous for the SCR activity. Fig. 1a shows that the catalyst with the optimum loading and composition (4.5 wt% FeVO_4) is activated by elevating the calcination temperature. This activation was investigated by means of XRD, BET, DRIFTS and XANES.

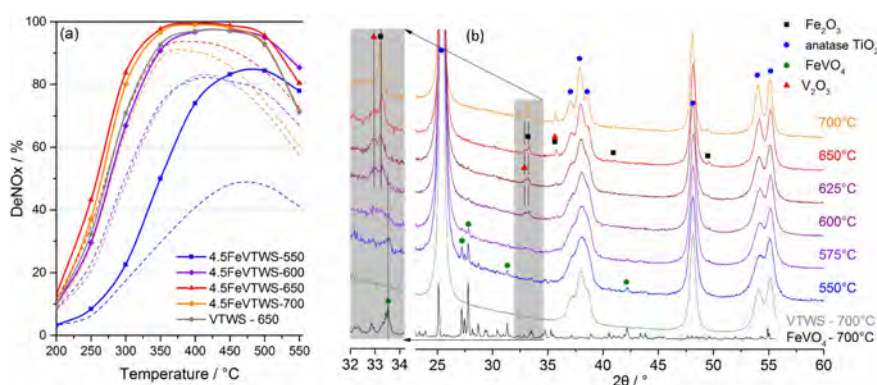


Figure 1 a) DeNO_x activity and b) XRD of 4.5 wt% FeVO_4 /TWS and VTWS calcined at different temperatures

Structural characterization by XRD (Fig. 1b) shows that the temperature activation of the supported FeVO_4 is accompanied by its phase transformation. Surprisingly, no FeVO_4 phase is detected above 650°C but Fe_2O_3 is formed. In contrast, the unsupported FeVO_4 is stable at 700°C . The interaction with TWS seems to promote the decomposition of FeVO_4 . We further provide strong evidence that the active species responsible for NH_3 -SCR in a FeVO_4 /TWS catalyst is not FeVO_4 but VO_x species that possess similar coordination environment to the VO_x species of conventional V-based catalysts. Despite the phase decomposition, a very active and thermally stable SCR catalyst was obtained after thermal activation.

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Direct conversion of cellulose into HMF

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Transformation of lignocellulosic biomass into commodity chemicals is of growing importance as alternative feedstock to petrochemical derived compounds, however, chemical transformations of lignocellulosic substrates that afford valuable platform chemicals remain challenging. Ionic liquids (ILs) have been explored as alternative solvents for 5-hydroxymethylfurfural (HMF) production as they are potentially capable of dissolving and deconstructing biomass and also of simultaneously catalyzing reactions. Cellulose possesses significant thermal and chemical stability, and its transformation into valuable products cannot be considered as a simple process. Herein, we describe a study concerned with the application of IL-CrCl₂ systems in which the introduction and configuration of functional groups pave the way towards the rational design of IL systems with tunable properties. We demonstrate that modification of IL and addition of task specific groups affects the reaction rate and allow us to significantly suppress side products formation. NMR study and stability test confirmed the importance of introduced groups. The transformation of more complex carbohydrates, including cellulose, has also been studied and good yields of HMF were obtained, whereas no product was observed when other ionic liquids were employed, demonstrating the efficacy of the new system.