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Taming the Reactivity of Nickelate/Cation(s) Ion Pairs in Catalysis: DFT Insights

Metal-ate complexes are highly reactive species that can facilitate elementary steps in catalysis, such as oxidative addition or highly hindered C-C bond creation. Controlling their formation and tuning their reactivity is appealing, but this requires a detailed picture of the parameters governing their structure and their reactivity (ligand, solvent, additives, …). Our collaborators have recently developed a cyanoalkylation of ketone derivatives catalysed by a well-defined Ni(II) anionic catalyst (**Fig.a**).**[1]** The reaction involves the formation of nickelate-cation (Cat+) ion-pairs together with a ketenimine (N-coordination) / cyanoalkyl (C-coordination) equilibrium. This is a versatile and realistic model system to understand the structure - reactivity relationship in that class of catalytic active species.

The N- and C-coordination of cyanoalkyls is often described as a structural continuum.**[2]** Based on DFT modelling, we analysed the interactions between the substrate and alkali- or transition-metals complexes (Gaussian16/B3PW91-D3BJ/SMD(THF)/6-31++G\\/SDD(Ni,Cs) & associated basis sets). Alkali-metals favour N-metalation by displacing lone pairs on the nitrogen atom - similarly to an electric field (**Fig.b**). With transition-metals, the formation of more covalent M-C bonds (M = Ni, Cu catalysts) acts as a driving force, which can be modulated by tuning the ligand.

Based on these results, the cyanoalkylation mechanism is examined with emphasis on the nature of the cation (alkali-metal vs. ammonium). Compared to systems in the literature, the nickelate catalyst reduces the activation energy for C–C bond formation sixfold.**[3]** Preliminary results suggest that the Cs^+ cation arising from the base, does not affect the reaction kinetics or thermodynamics of the reaction (**Fig. c**). Current efforts focus on probing interactions between the nickelate and alkylammonium cations, featuring different steric and electrostatic properties for enantioselective applications in catalysis. These results will improve our understanding of chemical systems that are governed by environment effects (solvation, ion-pair formation, alkylammonium cation, …) and pose a modelling challenge.

[1] A. Cofinet *et Al*, *Adv. Synth. Catal.* **2023**, *365*, 156

[2] X. Yang, F. Fleming, *Acc. Chem. Res.* **2017**, *50*, 2556

[3] A. J. Canty *et Al.*, *ACS Catal.* **2016**, *6*, 60–68

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