

# On the Role of Anions in Solid Catalysts with Ionic Liquid Layer (SCILL) for the Selective Hydrogenation of Highly Concentrated Acetylene Streams

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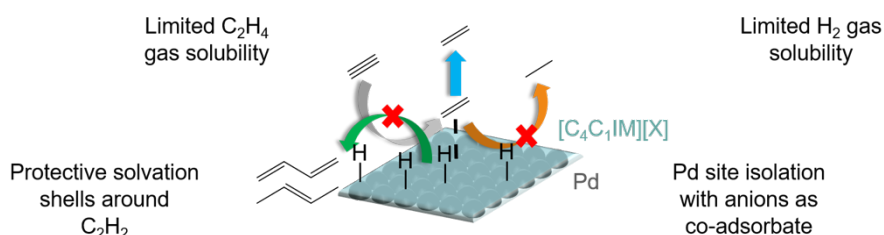
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Ethylene is an important platform molecule in the chemical industry. Conventional production via the steam cracking of naphtha involves the usage of fossil fuel feedstocks and significant emission of greenhouse gases.<sup>1,2</sup> One sustainable alternative represents the electric plasma-assisted pyrolysis of methane, whereby sustainable feedstocks like biogas or hydrogenated carbon dioxide and renewable energies can be applied. The obtained ethylene streams contain, however, much higher concentrated acetylene impurities ( $\geq 15$  vol.-%) than from the steam cracking of naphtha ( $< 2$  vol.-%), which have to be selectively converted to ethylene before further usage. The high exothermicity of the hydrogenation reaction as well as increased oligomerisation tendency at such high concentration require much more robust catalysts to maintain high selectivity and stability on-stream than currently developed for low acetylene concentrations.<sup>3,4</sup>

In this study, we have modified an intrinsically non-selective, porous palladium catalyst with imidazolium based ionic liquids to so-called solid catalysts with ionic liquid layer (SCILL) varying among ten different anions and investigated their performance in the selective hydrogenation of such highly concentrated acetylene streams under industrially relevant conditions ( $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{H}_2$  1:1:5, WHSV 45 000  $\text{cm}^3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ , 120 °C, 10 bar).

Deposition of imidazolium based ionic liquids onto the porous palladium catalyst significantly increases average ethylene selectivity over 20 h on-stream from 0 up to 82% by reducing full hydrogenation (from 75 down to 7%) and oligomerisation side-reaction (from 25 down to 11%). Most of the so-called SCILLs are thereby clearly outperforming more conventional Pd-Ag catalyst, previously optimized for this reaction<sup>4</sup>, with regard to selectivity and lifetime. The performance of SCILLs reveals to be highly dependent on the choice of anion determining decisive parameters of the ionic liquid. Varying feed gas composition, temperature, ionic liquid loading, cations and investigating surface phenomena via XPS a very comprehensive understanding about the underlying phenomena was obtained (summarized in Figure 1): Limited gas solubility of hydrogen in the ionic liquid layer seems to reduce full hydrogenation, while stronger and bulkier solvation shells around the acetylene molecule are likely to avoid oligomerisation processes. Surface analysis furthermore suggests strong anion coordination to

the palladium surface, likely creating a similar active site isolation as in the case of Pd-Ag alloyed catalysts.



**Figure 1.** Model of a palladium catalyst modified with imidazolium based ionic liquids to solid catalysts with ionic liquid layer (SCILL) illustrating possible selectivity enhancing effects in the selective gas-phase hydrogenation of highly concentrated acetylene streams.

[1] H. Zimmermann in Ullmann's Encyclopedia of Industrial Chemistry, Ethylene, Vol. 13, VCH, Weinheim, 2012, pp. 465-529; <sup>2</sup> X. Cao et al., *Mol.* 2023, 28, 2572; <sup>3</sup> E. Delikonstantis et al., *Fuel Process. Technol.* 2018, 176, 33-42; <sup>4</sup> K. Kley et al., *Catal. Sci. Technol.* 2023, 13, 119-131.