Disproportionation of Silyl Formates, a Novel Strategy for Renewable Methanol Production

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Methanol (CH_3OH) is a useful C_1 building block employed in the chemical industry as precursor of important commodity chemicals such as formaldehyde, acetic acid or light olefins via the methanol-to-olefins (MTO) process. Nevertheless, the current methanol production methods is negatively impacted by the use of fossil resources. The production of CH_3OH would therefore strongly benefit from the advent of more sustainable processes like the six-electron reduction of CO_2 by hydrogenation, for example. An alternative strategy has recently emerged to generate CH_3OH from CO_2 via the intermediacy of formic acid (FA) as a C–H bond shuttle. At the onset, CO_2 is first reduced into FA by a relatively facile and intensively studied two-electron reduction (e.g. electroreduction). Subsequently, CH_3OH is produced by the disproportionation of FA. Under standard conditions, the competitive dehydrogenation and the targeted disproportionation of FA however display similar energy balances. To overcome this inextricable hurdle, we have thus sought a novel disproportionative route to methanol that suppresses the competing dehydrogenation pathway, while remaining attractive from the viewpoint of renewability. Towards that goal, we present a novel strategy based on the high-yielding catalytic disproportionation of silyl formates (HCO_2SiR_3) to methoxysilane (CH_3OSiR_3) and CO_2 followed by the release of free CH_3OH and the complete recycling of the silicon-containing byproducts generated throughout the process.