Reactivity and selectivity of homo-coupling reactions driven by surface orientation and temperature

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Abstract: On-surface synthesis approach allows exploring original reaction pathways between small aromatic precursors confined to the surface of single crystal metals. Here we show that an indacene derivative reacts with itself on silver surfaces in different ways, through a Knoevenagel reaction or/and an oxidative coupling, and leads to the formation of a variety of new molecular compounds and covalently-linked 1D or 2D networks. In the case of indacene derivatives adsorbed on Ag(110) surface kept at 300°C it was found that functionalized 1D organic nanoribbons grow only via oxidative coupling which has never been observed in traditional solvent-based chemistry. Thus high reactions selectivity is induced by substrate orientation whereby the nanoribbon length can be further increased by annealing to higher temperature. In contrast to Ag(110), the reactions selectivity between indacenes deposited on Ag(100) can be finely controlled by the temperature: Knoevenagel-type coupling is mainly obtained for 280 °C annealing, while for 350°C both coupling types are allowed. Meanwhile, disordered 2D polymers on Ag(111) surface are formed via both couplings at activation temperatures as low as 200°C suggesting that the substrate orientation drastically increases reactivity in this case. The different structures were characterized by scanning tunnelling microscopy (STM) together with X-ray photoelectron emission spectroscopy (XPS). Signatures of the covalent coupling in the molecular species were also evidenced with high-resolution electron energy loss spectroscopy (HREELS), and supported by density functional theory calculations.

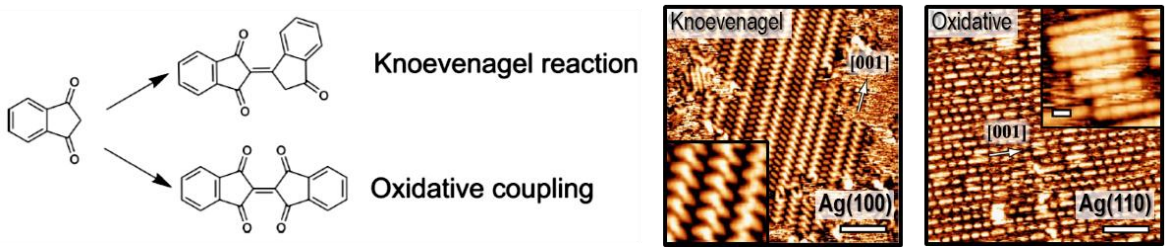

Figure: On-surface reaction mechanisms for indacene derivative. STM images of dimer covalent structure formed via Knoevenagel reaction on Ag(100) and 1D polymeric structures obtained after oxidative coupling on Ag(110) kept at 280°C and 300°C, respectively. Scale bars: 6 nm

References:

[1] N. Kalashnyk et al. On-surface synthesis of aligned functional nanoribbons monitored by scanning tunneling microscopy and vibrational spectroscopy. Nature Commun. 8, 14735 (2017)

[2] N. Kalashnyk et al. The orientation of silver surfaces drives the reactivity and the selectivity in homo-coupling reactions. ChemPhysChem 19, 1802 (2018)