

ABSTRACT

Towards Low-Temperature Heterogeneous Hydrogenation of Carbonyl Compounds: Molecular Systems for Reversible Hydrogen Storage

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Hydrogenation of carbonyl compounds to alcohols is an important step in many technological applications, including the emerging molecular systems for reversible hydrogen storage. This class of reactions is challenging as it requires the activation of a stable C=O bond, typically occurring under harsh conditions. There is an ongoing discussion on an alternative theoretically predicted pathway, comprising two consecutive steps: keto-enol tautomerization of the carbonyl compound to its enol counterpart followed by hydrogen insertion into the C=C bond. Both steps were predicted to proceed via significantly lower barriers than for direct hydrogen insertion into the C=O bond. The major challenge of this mechanism is the low stability of enols that – if not stabilized – readily convert back to ketones.

In this study, we present our recent investigations on formation of enol species from carbonyl compounds acetophenone, acetyl pyridine and butanal and their stabilization via hydrogen bonding with neighboring carbonyls.^{1,2} By employing a combination of IRAS, STM and molecular beam techniques, we demonstrate the proof-of-principles experiments confirming the possibility of their low-barrier hydrogenation proceeding via keto-enol tautomerization as a first step. The enol species become stabilized on surfaces in form of ketone-enol dimers or ketone-enol-enol trimers via strong hydrogen bonding between the C=O group of the ketone form and the OH-group of the enol species. The enol species in the ketone-enol dimer can be hydrogenated already at cryogenic temperatures, suggesting drastically reduced activation barrier as compared to direct hydrogenation of the carbonyl group. The stabilization of enols in form of ketone-enol dimers or ketone-enol-enol trimers turns out to be the crucial reaction step, allowing the enol-containing reaction intermediate to enter the second reaction step – hydrogenation of the olefinic bond.

Obtained atomistic-level insights in low-barrier hydrogenation of carbonyl compounds provide important information on the elementary reaction steps of this highly promising class of reactions for hydrogen storage. Related phenomena can be employed for controlling keto-enol tautomerization and enol stabilization via mutual lateral interactions on functionalized catalytic surfaces for the broad range of aldehydes and ketones to enable their low-barrier hydrogenation.

1. Schauer mann, S., ACS Catal. 2023, 13, 13423
2. Haugg, Ph. A., ACS Catal. 2024, 14, 10022