The mechanism of CO$_2$ reduction over Pd/Al$_2$O$_3$: a combined transient DRIFTS and steady state isotope transient kinetic analysis (SSITKA)/operando FTIR investigation

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Understanding the critical steps involved in the heterogeneous catalytic CO$_2$ reduction has attracted a lot of attention recently. In order to fully understand the mechanism of this reaction the determination of both the rate-determining steps and reaction intermediates are vital. Transient DRIFTS/MS measurements provided invaluable information on the nature of surface species and on their reactivities under various reaction conditions. Steady-State Isotopic Transient Kinetic Analysis (SSITKA) is one of the most powerful techniques used to investigate the elementary steps under steady-state reaction conditions. This technique provides valuable information on mean resident lifetime of surface intermediates, surface concentrations of adsorbed reactant species and an upper bound of the turnover frequency. Coupling SSITKA with operando-FTIR spectroscopy allows us to discriminate between active and spectator species present on the catalytic surface under steady state reaction conditions. In the present work operando SSITKA experiments coupled with transmission FTIR, mass spectrometry (MS) and gas chromatography (GC) were performed to probe both the chemical nature and kinetics of reactive intermediates over Pd-Al$_2$O$_3$ catalysts and provide a clear mechanistic picture of the CO$_2$ hydrogenation reaction by revealing the rate-determining steps for CH$_4$ and CO production. These studies revealed that the rate-determining step for CO formation is the reduction of adsorbed formate, while that for CH$_4$ formation is the hydrogenation of strongly adsorbed carbonyls. The balance of the hydrogenation kinetics between adsorbed formates and carbonyls governs the selectivities to CH$_4$ and CO. This knowledge can be applied to design catalysts that are able to achieve high selectivities to desired products.