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Mechanistic study of the palladium-catalyzed ethyne hydrogenation by the Temporal Analysis of Products technique

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ABSTRACT

The gas-phase hydrogenation of ethyne over Pd/Al_2O_3 is studied using the Temporal Analysis of Products (TAP) reactor, leading to valuable insights into the reaction mechanism. The exceptional time resolution of this transient technique enables to capture the hydrogenation of the carbon–carbon triple bond *via* the sequential addition of hydrogen. Hydrogen/deuterium exchange experiments demonstrate the dissociative and reversible adsorption of H_2 on palladium. Conversion and selectivity change at early stages of the reaction as a consequence of the formation of a stable carbide layer. The alkene/alkane ratio was markedly higher in TAP compared to reported flow data, due to the mbar pressure operation of the technique. In this regime, the formation of subsurface hydrogen is unfavorable, enabling the assessment of the sole effect of reactants coverage on the product distribution, that is, in the absence of unselective hydride phases. Mechanistic aspects related to the use of carbon monoxide as a selectivity enhancer are also discussed.

1. Introduction

The practical relevance of the catalyzed partial hydrogenation of carbon–carbon triple bonds in the purification of olefin streams [1,2] and in the manufacture of fine chemicals [3,4] has led to intensive efforts in order to improve its fundamental understanding. Many catalytic systems have been studied [2], with particular focus on palladium [5]. The influence of four main aspects impacting on the catalytic performance has been investigated by means of experimental and molecular modeling approaches: (i) the surface/subsurface chemistry [6–9], (ii) the particle (ensemble) size [5,10,11], (iii) the support [11–13], and (iv) the use of modifiers, such as additional metals [5,14–20], ligands [21–23], and continuous CO supply [1,5,8]. However, some of these aspects are tightly inter-related, making it intricate to isolate individual contributions. For example, subsurface carbides and hydrides play an important role on determining the activity and selectivity of Pd catalysts in alkyne hydrogenation [6,8]. However, the competitive effects of the two subsurface species are tightly related to the size of the palladium particles. Carbides are preferably formed on step sites, that is, more favorably in smaller particles, while large palladium ensembles favor hydride formation [8,10,11]. Palladium hydride phases are easily formed in ambient-pressure catalytic tests and promote the over-hydrogenation of the alkyne. A high hydrogen coverage and hydride phases likely co-exist in a working catalyst and due to this, the individual contribution of surface and subsurface species to the product distribution cannot be easily ascertained. Novel techniques providing new insights into the reaction mechanism or resolving equivocal conclusions in existing studies will strengthen the understanding of the partial alkyne hydrogenation, with the ultimate goal of designing improved catalysts.

The Temporal Analysis of Products (TAP) reactor is a transient technique whose operation is based on delivering tiny amounts of reactants in the form of pulses (*ca.* 0.1–100 nmol) to the catalyst with a background pressure of 10^{-8}–10^{-9} mbar [24–27]. The main advantages of the TAP technique for mechanistic and kinetic investigations of gas–solid reactions are the millisecond time resolution, the use of practical catalysts, and the excellent temperature control. Oxidations of hydrocarbons or inorganic substrates (*e.g.* NH_3, HCl) over pure metals, alloys, and metal oxides comprise the main family of (exothermic and fast) reactions that have profited from the unique features of this dynamic method in the last three decades [28–31]. In contrast, TAP reactor studies of gas-phase hydrogenations are scarce. Moser et al. [32] derived mechanistic aspects of the tetrahydrotiophene desulfurization on sulfided Co-Mo/γ-Al_2O_3, Rothaemel et al. [33] monitored the formation of formyl species upon interaction of CO and H_2 on Pd/γ-Al_2O_3, and Lafyatis et al. [34] applied moment analysis of the transient responses to estimate surface reaction rates of benzene hydrogenation over Pt/SiO_2. More recent TAP investigations involving molecular hydrogen comprise

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