

The Carbonaceous Ad-Layer as Rate Controlling Factor in CO/H₂ Catalysis

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Research Scope and Objective

With the exception of methanol synthesis catalysts, CO/H₂ converting catalysts are comparatively inactive. Surface analysis often reveals the formation of substantial amounts of carbonaceous surface residues. Finally, a recent isotopic transient-kinetic study of three CO/H₂ converting catalysts (Ni, Co, Ru) revealed that during steady state catalysis the surface coverage in reaction intermediates is low (2). The objective of this program is to assess to what extent the aforementioned three observations are casually related: do side products control the coverage in reaction intermediates?

Description of Research Effort

Research focusses on the isotopic transient-kinetic information which results from abruptly switching the isotopic composition of the reactants, e.g., $^{12}\text{CO}/\text{H}_2 \longrightarrow ^{13}\text{CO}/\text{H}_2$ (1, 2, 3). The rate of penetration of the "new" isotope in the ad-layer and in the products allows for determination of the coverage (θ) and reactivity (k, s^{-1}) of reaction intermediates. An Initiation Grant from the University has been utilized to set-up a system in which (1) the isotopic change in reaction ambient is sharply defined (rise time = 1s), and (2) the resulting ingrowth of the new isotope in product is being followed with a high-transmission Quadrupole Mass Spectrometer (Extra Nuclear). This system currently is operational, and it performs significantly better than the one utilized in our preliminary study (2).

As DOE-ER funding formally start on September 1, we utilized a part our Initiation grant to start this program. Specifically, we measured reaction-intermediate coverages on Raney Nickel and Ni-SiO₂ under H₂/CO = 60 and in the very initial stage of exposure of the catalyst to (very hydrogen rich) sungas. These conditions supposedly lead to a "clean" catalyst surface. Surprisingly, the we find that the coverage in reaction intermediates, under these conditions, is of the order of 0.02 - 0.04 only. We consider this to be a preliminary indication that, in this specific case, the (low) coverage in reaction intermediates is not being caused by side products.

Future Research

What has been described above is the start of an investigation in which variations of $\theta_{\text{intermediates}}$ with nature of the catalyst, reaction ambient, time-on-stream and abundancy of a carbonaceous overlayer will be assessed systematically.

References

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