Comments

Comments on Catalytic Probe of the Surface Statistics of Palladium Crystallites Deposited on Montmorillonite

In a recent issue of this journal Veisz et al. published a paper on the catalytic probe of the surface statistics of Pd/montmorillonite catalysts (liquid-phase room-temperature hydrogenation of styrene).[1] The reader may find several problematic points in the paper. The problems and attempts to resolve them are given in this comment. The answers are mostly contradictory to those described in the commented paper and they are based on the present author's hands-on experience with liquid-phase hydrogenation of various olefins (cyclohexene, 1-hexene, and others) over supported transition metal (Pt, Pd, Rh) catalysts[2,3] as well as articles published on related studies throughout the scientific literature.

The published method of preparation of Pd/montmorillonite catalysts with wide-ranging particle size is very useful indeed. It allows more control over the particle size and distribution than the other traditional methods. Hopefully, the mean particle size and the particle size distribution have been determined on counting and measuring a statistically significant number of particles (these numbers are not given in the paper; electron microscopy was used).

The choice of the geometric body thought to be representative for the Pd/montmorillonite catalysts was made on the basis of a high-resolution electron microscopy (HRTEM) measurement. It was found to be a cubo-octahedron and surface statistics were made purely on geometric considerations. This choice was not made on the HRTEM image of the "real" catalyst, but on that of the hydrosol. It is well-known, however, that during deposition many changes can occur and, probably, the regular geometric body undergoes considerable distortion. Even if one accepts that the cubo-octahedron is a good model, deposition onto an "ideal" flat surface makes large portions of the metal crystallites unaccessible for the reactants. This problem is verbally treated in the work, but it is also stated that the results are not influenced significantly. It is surprising, especially at low particle sizes, where large portions of the defect sites will become unavailable.

The reader may ask whether surface statistics for an unreacted ideal catalyst remains valid for a catalyst under reaction. The question is not at all philosophical since it is known from surface science studies that the adsorbed material very often causes surface reconstruction. It was proposed a long time ago by Taylor that the reactant and the catalyst cannot be taken as separate entities.[4] The reacting compound transforms the surface of the catalyst; it makes the catalytically active site for itself. Since then, many experimental evidences for the validity of this proposal have accumulated and it is generally accepted in the catalysis community that the catalyst is not rigid, but flexible; it makes the surface best suited for the reaction together with the reactant(s).[5] Thus, the answer to the question posed in this paragraph is unequivocally no. The reacting surface, especially in the conversion of olefins where part of the active sites is proven to be hydrogen-rich carbonaceous residues, cannot be represented by geometric forms and any surface statistics of the unreacting catalyst.

It also can be asked if it is certain that the dissociation of H_2 is rate-limiting. It is generally agreed that the olefin coverage is constant (close to full occupancy of the surface) up to large conversions leading to zero reaction order in the olefin. However, there is no general agreement on the dissociation of H_2 being rate-limiting and there is no experimental evidence for this in the commented paper either.

It can be asked as well whether it is true that liquid-phase hydrogenations are structure-sensitive in general, while they are structure-insensitive in the gas phase. Literature concerning this topic is vast; therefore, I have no intention of discussing it exhaustively. For giving the answer "not true", it is enough to cite a couple of seminal papers. Boudart and co-workers published a series of articles on the liquid-phase hydrogenation of cyclohexene over a variety of transition metal (Pt, Pd, Ni) catalysts.[6] They found a complete lack of structure sensitivity. Butt and co-workers found, however, that propylene hydrogenation in the gas phase, although not dramatically, is structure sensitive.[7]

To summarize, in the paper of Veisz et al. an appreciable method for the preparation of Pd/montmorillonite catalysts with preplanned particle size and relatively narrow particle size distribution is given; however, the applicability of the catalytic probe for surface statistics, given in the title of the paper, is questionable. The approach contains fundamentally vague points and the interpretation is based on an outdated picture of how a catalyst works.

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