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

Sir, we have read your criticism on our catalytic probe[1] with interest. In this rebuttal, we wish to address the major issues via which you cast doubt on the conclusions of our paper.

We reported on a novel preparation technique which provided a series of low-loaded Pd/montmorillonite catalysts containing cubo-octahedral Pd particles.[1] The dispersion *D* of the metal was computed as a function of the mean diameter *d*, in terms of terrace sites (face atoms only), defect sites (edge and corner atoms), and the total number of (terrace plus defect) surface sites. Unexposed Pd atoms in contact with the underlying support were taken into consideration on a statistical basis. The turnover frequency TOF should be constant, independent of particle size, if the correct ensemble of surface sites is selected for the calculation of *D*.[2,3] This led us to conclude that it is the low coordination edge and corner atoms which are responsible for the activity of the catalysts in the liquid-phase hydrogenation of styrene to ethylbenzene under mild conditions.

In contrast to your remarks, the title and the geometric formalism of the catalytic test method described in ref 1 have been well-established both theoretically[2] and experimentally[3] in excellent papers by outstanding scientists.

The conflict between us basically stems from the limitations of the outdated experiments you cited, for example, ref 4, which tend to lead to inadequate conclusions. The question to be first considered is not how supported metal catalysts work but how the catalysts should be selected for a systematic study on the fundamental aspects of structure sensitivity. Since the interpretation of the results of the hydrogenation of olefins in the liquid phase is inevitably influenced by the nature of the catalysts chosen for such studies, it is of interest to compare the catalyst samples and the characterization methods in our paper[1] with those in your paper.[4]

The preparation of supported metal catalysts differing only in the size of the metal crystallites, and not in other respects, is a challenging task. We attempted to approach such an idealized situation.[1] The support material was of the same kind (montmorillonite); the Pd loadings were identical; the particles displayed narrow size distributions (TEM) and covered the size range optimal for the testing of structure sensitivity;[2,3] the dominant morphology was found to be cubo-octahedral (HRTEM); and essentially the same preparation methodology, a controlled growth technique, was applied. In contrast, the samples in your series of Pd/SiO_2 catalysts[4] had different silica supports; they had different particle loadings; the mean diameters, the size distributions, and the morphologies were not at all investigated; and the morphologies (including surface site distributions) of the Pd crystallites must have been different because the particles were prepared by conventional methods: impregnation and ion exchange. In our work,[1] *D* was justified by the catalytic reaction itself. In your work,[4] *D* was derived from CO chemisorption on Pd with an arbitrarily chosen stoichiometry of 1:1, and further the point was neglected that the number of sites capable of binding CO molecules may differ significantly from the number of sites on which the reactions you studied, the hydrogenations of cyclohexene and 1-hexene, take place.

Although impregnation metal catalysts are, and will remain, of great practical importance, they are not ideally suited for a systematic study on structure sensitivity when the samples are ill-defined and/or they are not in the corresponding states. It is not surprising that your TOF displayed a maximum dependence on *D*. This trend could possibly be attributed to a combination of the various factors you mentioned in your comments, but most importantly, it could be due to the differences in history (morphology) of the metal particles, which you completely ignored. An attempt was made to minimize such factors in our study.[1] If side effects had been significant, our catalytic probe would have failed.

The preliminary results of our poisoning experiments are fully consistent with the conclusions in ref 1, but are in contrast with your observations. You reported in ref 4 that the number of surface atoms deactivated by one poison molecule (CCl_4) did not correlate with *D*. We applied CS_2, a strong poisoning agent. A linear relationship was found between the rate of hydrogenation and the fraction of defect sites poisoned, and hydrogenation ceased when the defect sites were quantitatively covered by poison molecules. These experiments will be reported on in a forthcoming paper.

The value of the HRTEM image in ref 1 should not be underestimated; this provides the atomic resolution of a cubo-octahedral Pd particle deposited from the hydrosol onto a grid (such measurements cannot be conducted in situ in the liquid phase). Atomic resolution of the particles deposited on the clay could not be achieved technically. However, there is no a priori reason to believe that the deposition of the preformed Pd crystallites would cause a significant distortion of their cubo-octahedral shape when the support material is the parent clay and not the grid. Our catalytic probe did not justify either a selective distortion of this kind or a crystallographic rearrangement of the metal particles involved in the reaction. Crystallites grown under controlled conditions, and magic-number full-shell particles in particular, display a substantially higher thermodynamic stability than that of random particles with irregular shapes and high surface imperfections.[5,6]

Although the S/L interface is in many respects different from the S/G interface, the two kinds of interfaces are treated indiscriminately in your remarks. Supported

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metal crystallites in colloidal suspensions are not the typical targets of surface science studies. Local surface restructuring, if any, of metal particles during exothermal events (adsorption, catalytic reaction, and high-energy irradiation) is more likely to occur in low heat conduction surroundings (vacuum and gas phase)[6] than in a liquid medium, which acts as an efficient heat sink. Your arguments concerning the rearrangement of surface sites and the formation of carbonaceous deposits are irrelevant because the kinetic curves for the conversion of styrene to ethylbenzene were found to be linear throughout,[1,7] and this finding precludes the occurrence of gradual activation or deactivation of the catalysts during the reaction.

We agree that the catalyst surface and the reactant should not be treated as separate entities, certainly with concern to the reaction. However, they should be clearly distinguished after desorption of the product, which leaves the surface essentially unchanged for further transformations. Our catalysts did not display any loss of activity in repeated use.

Finally, what we claimed was that, under mild conditions, it is the activation of H_2 which is the rate-determining step of the liquid-phase hydrogenation of styrene to ethylbenzene over the Pd particles.[7] The rate depends on the concentration of dissolved H_2, which in turn depends on the H_2 pressure applied.[7,8] At low pressure/solubility, the reaction follows zero-order kinetics with respect to styrene; there is a deviation from this at high pressure/solubility.[7]

It is trivial that the thermodynamic properties of an ideal gas are simple as compared to those of (a mixture of) real gases. By way of analogy, the catalytic behavior of metal particles of uniform size and shape are less complex than those of randomly generated ones. This remark is not merely philosophical, but from a practical aspect relates to the advantages of applying smart systems in fundamental studies on interfacial phenomena, including catalysis.[6]

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