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LETTER TO THE EDITOR

Response to "Comment on 'Influence of Hydrogen Chemisorption on the Surface Composition of Pt–Rh/Al_2O_3 Catalysts,'" by J. J. van der Klink and J.-Ph. Ansermet

van der Klink and Ansermet correctly point out that in our analysis of ^{1}H NMR data for the H/Pt–Rh/SiO_2 system (1), Eq. [3] is not very general. Indeed, much of the discussion in our paper was on this very point. However, it must be noted that regardless which model (local or nonlocal) is applicable, both Eqs. [3] and [4] in Ref. (1) indicate that the net proton Knight shift of H on the alloy is related to the surface composition of the alloy. Furthermore, for highly disordered systems (like our samples) the density of states can always be expressed as Eq. [4] for all layers of the system, in the bulk or in the surface, in accordance with the quasicrystalline approximation. We agree that direct comparison of the ^{1}H shift of adsorbed hydrogen with the ^{13}C shift in adsorbed CO is questionable since the two adsorbates interact with the metal surface in different ways. For example, the Knight shift arises out of a finite density of bonding states at the Fermi surface. While the primary bonding interaction of hydrogen is via the *s* orbital of hydrogen, CO has both a sigma bond and "back" donation of conduction electrons to the antibonding $2\pi^*$ orbital.

It should be noted that our analysis does not suggest that the surface of the Pt–Rh particles is significantly "depleted in platinum" but that it is much closer to the overall particle composition. Rather, we do claim that the surface composition is depleted in Pt *relative to what it would be in the absence of an adsorbate.* It is also important to recognize that the influence of an adsorbate on the surface composition of an alloy is very much dependent on the nature of the adsorbate itself. It is unlikely H and CO have identical variations in the heat of adsorption between Pt and Rh.

REFERENCE

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