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LETTER TO THE EDITOR

Comment on “Influence of Hydrogen Chemisorption on the Surface Composition of Pt–Rh/Al$_2$O$_3$ Catalysts”

Some time ago in this journal, Pruski and co-workers reported (1) a proton NMR study of hydrogen chemisorption on supported Pt/Rh catalysts of varying overall compositions Pt$_{1-x}$Rh$_x$. They argue that under conditions of rapid exchange of hydrogen over the different sites of a fully covered metal surface, the observed shift of the hydrogen NMR signal should be given by

$$\delta_{\mathrm{obs}} = (1-y)\delta_{\mathrm{Pt}} + y\delta_{\mathrm{Rh}}, \qquad [1]$$

with δ_{Pt} and δ_{Rh} independent of y, and where the composition of the surface is taken as Pt$_{1-y}$Rh$_y$, with y possibly different from x. In a plot of the experimental values of δ_{obs} as a function of overall Rh content x, the points at intermediate concentrations fall below the straight line that joins the data for $x=0$ and $x=1$ (see Fig. 1); from this the authors conclude that the surface is depleted in platinum ($x<y$) and determine a relation between x and y. They imply that in (2) NMR data for ^{13}CO adsorbed on Pt/Rh catalysts (see Fig. 1) have also been interpreted using Eq. [1]. We would like to add some remarks to their analysis.

It is correct that the authors of (2) concluded from their NMR experiments that $x<y$, but that conclusion was not based on the ^{13}CO shift data in their Fig. 11. Indeed, in the discussion of that figure, they say that “it would be tempting to interpret [the ^{13}CO shifts] as an indication that Rh segregates to the surface,” but that their other results “show that this interpretation is erroneous.” For the alternative explanation proposed by these authors, we refer to the original paper (2).

Savargaonkar *et al.* (1) have also mentioned that the interpretation of the observed shifts is not straightforward. They consider two limiting cases: (I) a localised model where the value of the NMR shift of a given proton is independent of x or y, and is only determined by the identity of its closest metal neighbour atom (Pt or Rh); and (II) a nonlocal picture where the shift depends on the local density of states at the Fermi energy $\rho(E_{\mathrm{F}})$ on the metal surface sites. For the case (II), they cite an equation for the density of states given by Bennemann and co-workers (3), in the form

$$\rho_\lambda(E) = (1-y)\rho_{\lambda,\mathrm{Pt}} + y\rho_{\lambda,\mathrm{Rh}}, \qquad [2]$$

where λ is a parameter that distinguishes different atomic layers ($\lambda=1$ denotes the surface layer, $\lambda=2$ the subsurface layer, and so on). In their use of Eq. [2], however, Savargaonkar *et al.* (1) treat $\rho_{\lambda,\mathrm{Pt}}$ and $\rho_{\lambda,\mathrm{Rh}}$ as independent of y, which is obviously not compatible with the theoretical considerations in (3). Also the Knight shifts of ^{195}Pt and ^{103}Rh in the bulk ($\lambda \gg 1$) are determined by $\rho_{\lambda,\mathrm{Pt}}$ resp. $\rho_{\lambda,\mathrm{Rh}}$. If these density of states were independent of x, the NMR frequencies of ^{195}Pt and ^{103}Rh should be independent of composition, which is not the case (4). The situation for $\lambda=1$ is not known for Pt/Rh, but data are available for ^{195}Pt NMR in Pt/Pd small particles (5). If $\rho_{1,\mathrm{Pt}}$ were independent of y, the position of the “surface peak” in the small-particle NMR spectrum should be independent of composition, contrary to what is observed.

Therefore, the use of Eq. [1] would be justified only if model (I) is valid for the NMR of hydrogen on Pt/Rh catalysts. We think that this is unlikely, because hydrogen has no shielding core electrons of its own, so that its NMR shifts should rather closely reflect any changes in bonding related to changes in the nature of (at least) the closest neighbours to “the” binding site. Unless the surface is not a good approximation to a random alloy (e.g., when it consists of regions of pure Rh and pure Pt), the identity of

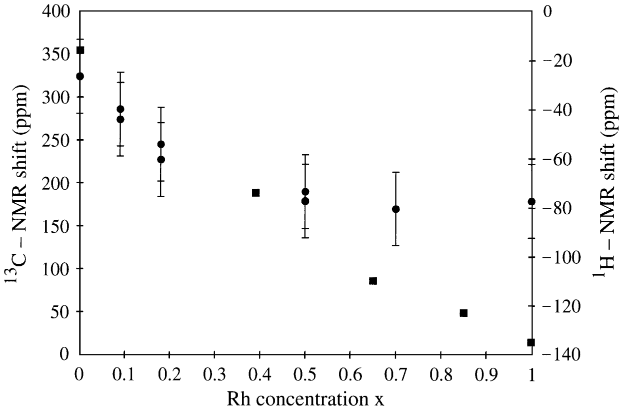

FIG. 1. Chemical shift data for adsorbates on Pt/Rh catalysts as a function of overall Rh concentration x. Squares and right-hand scale: ^{1}H, from Ref. (1). Circles and left-hand scale: ^{13}CO, from Ref. (2). In both cases the data points at intermediate concentrations fall below the line joining the $x=0$ and $x=1$ data; we argue that this does not allow one to conclude that for $0<x<1$ the surface is enriched in Rh.

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the neighbours will reflect the average composition of the surface, and one expects the shift to be governed by an equation similar to [2], with composition-dependent average densities of state on Pt and Rh sites. The validity of this model for chemisorbed CO has been shown by a ^{195}Pt–^{13}C double resonance experiment (2). In that case there is no reason that the data points of Fig. 1 should fall on a straight line when plotted as function of y instead of x. In conclusion, the validity of the method of data analysis used in (1) is certainly less general than its authors suggest.

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