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## This Week's Citation Classic 🖫

Tauster S J & Fung S C. Strong metal-support interactions: occurrence among the binary oxides of groups IIA-VB. J. Catalysis 55:29-35, 1978. [Exxon Research and Engineering Company, Linden, NJ]

This paper and the article by S.C. Fung, R.L. Garten, and me<sup>1</sup> reported drastic changes in the chemisorption properties of Group VIII noble metals when dispersed on the surfaces of titania and other reducible transition metal oxides. Possible trivial explanations were considered and rejected, and the results were attributed to a strong interaction at the metal-oxide interface. [The *SCI*<sup>®</sup> indicates that this paper has been cited in over 180 publications.]

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In 1970 the first experiments involving strong metal-support interactions were carried out at Exxon. Shortly before then I had become interested in the phenomenon of metal-metal bonding, in which cations bond to each other directly via overlap of their d orbitals. We had, in fact, studied the catalytic effects of this bonding in a class of compounds that included Mg<sub>2</sub>Mo<sub>1</sub>O<sub>8</sub>.

It was the work of the late Roland Ward and coworkers, however, that suggested the possible relevance of this chemistry to supportedmetal catalysts. They had found that titanium ions form metal-metal bonds with cations of platinum, rhodium, and six other transition metals.<sup>2</sup> Reading this paper conjured up the image of titanium ions acting as "live wires" at an oxide surface, able to interact with superjacent cations, or even metal atoms, via d orbital overlap.

I discussed this crude picture with Larry Murrell, who had a general interest in metalmetal bonding, and with Shun Fung, who was interested in ferroelectric titanates as supports. We decided to explore the catalytic and chemisorptive properties of noble metals on titanium-containing oxides. One of the most familiar properties of these metals is their ability to adsorb  $H_2$  (one H atom per suface metal atom), which is used to measure their dispersions. The result came as a complete surprise: Shun observed that the metals did not chemisorb  $H_2$ ! Bob Garten showed that trivial causes, such as encapsulation of the metal particles, could be ruled out, and he proposed that we replace the lackluster appellation "surface metal-metal bond" with "strong metal-support interaction."

I think our reports stimulated so much interest because they described a dramatic result in a simple experiment. For most metals the degree of chemisorption-suppression exceeded an order of magnitude; in contrast to catalytic effects, which are always subject to multiple explanations, chemisorption is basic. The evidence was persuasive that titania (titanium dioxide) was strongly interacting with the metal. Later, Murrell showed that one monolayer of titania dispersed on silica had similar properties.<sup>3</sup>

One branch of subsequent studies has been devoted to the effects of this interfacial chemistry on catalytic properties. CO-H<sub>2</sub> synthesis conversions have been the most extensively investigated, since activity and/or selectivity are frequently improved by these interactions.<sup>4</sup> For most hydrocarbon processes, activity is lowered, although selectivity for a desired product is sometimes increased. The reasons for these effects remain the subject of debate.

But it is the materials-science aspects of this research that I think are the most interesting. Here the involvement of surface scientists has been crucial. We now know of the convulsions that these interactions can produce, for example, reduced oxides swarming over metal surfaces in minutes at moderate temperatures.<sup>3</sup> Direct metal-cation interactions, which are the crux of these phenomena, have been demonstrated.<sup>6</sup> Such bonding can only be observed at an interface, and strong metal-support interactions are thus an example of how catalysis/surface science studies can enrich chemistry.

- Takatani S & Chung Y W. Strong metal-support interaction in Ni/TiO<sub>2</sub>: Auger and vibrational spectroscopy evidence for the segregation of TiO<sub>2</sub> on Ni and its effects on CO chemisorption. J. Catalysis 90:75-83, 1984.
- 6. Sadeghi H R & Henrich V E. Electronic interactions in the Rh/TiO, system. J. Catalysis. (In press.)

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Tauster S J, Fung S C & Garten R L. Strong metal-support interactions. Group 8 noble metals supported on TiO<sub>2</sub>, J. Amer. Chem. Soc. 100:170-5, 1978. (Cited 395 times.)

Dickinson J G, Katz L & Ward R. Compounds with the hexagonal barium titanate structure. J. Amer. Chem. Soc. 83:3026-9, 1961.

Murrell L L & Yates D J C, Strong metal-support interactions with ultradispersed rhodium. Stud. Surf. Sci. Catal. 7:1470-1, 1981.

Vannice M A & Garten R L. Metal-support effects on the activity and selectivity of Ni catalysts in CO/H<sub>2</sub> synthesis reactions. J. Catalysis 56:236-48, 1979. (Cited 175 times.)