# Submitted as a Letter to the Editor of Catalysis Letters

Dear Sir,

Under the above title, a Letter to the Editor has been published recently [1], discussing a brief report on metal-support interactions in methanol synthesis [2]. The first reference in [1] is ref. [3] that contains a brief perspective on the new material presented in [2]. As this note appeared under my signature in a periodical that is distributed privately, I believe that your readers should have a chance to read my note whose purpose was to bring attention to the work of ref. [2]. Here is the text of my note.

When a metal M interfaces with a semiconducting support S, the electrons move so that their chemical potential will reach the same value in both solids at equilibrium. This electron transfer, which is well known in physics, could also lead to a change in the rate at which either M or S catalyzes a reaction. Such an effect is called a metal-support interaction (MSI).

Much has been written on MSIs [see S.A. Stevenson, J.A. Dumesic, R.T.K. Baker, E. Ruckenstein, Eds., *Metal Support Interactions in Catalysis, Sintering, and Redispersion* (Van Nostrand Reinhold, New York, 1987)]. The classical phenomenon of MSI received renewed attention in 1979 following a study by Exxon scientists. They hypothesized that transition metal cations at a semiconductor support surface could interact strongly with adjacent metal atoms of the catalyst. The unusual chemisorptive and catalytic behavior of these systems was attributed to a strong metal-support interaction, or SMSI.

It is now accepted that a number of cases of SMSI can be explained by transport of the support material to the surface of the supported metal. In such cases, SMSI becomes a variation of the classical case of MSI due to the interfacing of the metal and the support, although details of the interaction still have to be understood.

An apparently clear-cut case of MSI where the catalyst is a thin layer of semiconducting oxide encapsulating a metal cluster has now been reported [J.C. Frost, Nature 334 (6183), (1988) 577]. A typical catalyst for methanol synthesis is depicted as clusters of a metal surrounded completely by an oxide catalyst. As a result of MSI, electrons from the metal interact with oxygen vacancies at the surface of the oxide. These are the sites where dihydrogen is dissociated, forming hydride ions. Insertion of CO then leads to a partially hydrogenated species that can be further hydrogenated readily until ($OCH_3$) is formed.

Desorption of $CH_3OH$ finally takes place with release of an electron to the metal. In this mechanism, the ease with which electrons can be exchanged between the metal and the oxide plays a determining role. Thus when the catalytic oxide is $ThO_2$, the catalytic activity ratio correlates with the work function of various metals: Ag, Cu, Au, Pd, and Pt. This catalytic activity ratio is defined as initial activity divided by activity after exposure to $CO_2$.

It will be very interesting to see the full publication of this work. Indeed, if methanol synthesis catalysts can be understood on the basis of electron transfer between the metal, say Cu, and the catalytic oxide, say ZnO, then commercial catalysts can perhaps also be improved by a design strategy based on the physics of MSI coupled with the solid-state defect chemistry of the catalyst. Also, new hydrogenation catalysts for other reactions may be discovered by other applications of the effect invoked in the case of methanol synthesis. This would signal a renaissance of the electronic theory of semiconductor catalysis that attracted a lot of attention in the 1950s because of its simplicity but was later abandoned because of its lack of predictive ability.

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## References

[1] V. Ponec, Catal. Lett. 11 (1991) 249.
[2] J.C. Frost, Nature 334 (1988) 577.
[3] M. Boudart, Catalytic Highlights 14, No. 4 (1988) p. 3.