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LETTER TO THE EDITOR

On the so-called "Junction effects" in methanol synthesis

Dear sir,

Recently, a paper appeared [1], which attracted much attention and was loudly aplauded [2]. It seemed on the first glance, that it had lead to the surprising predictions (for example, that Ag should be active in methanol synthesis), which were by the author confirmed. However, a close inspection of Frost's paper [1] did many doubts to rise and it is the purpose of my letter to initiate (hopefully) a discussion on the weak points in the theory.

Briefly summarised, Frost suggests that upon CH_3OH synthesis running, charged oxygen vacancies $[V_0^{++}]$ exist, which produce hydride (like) species from H_2. Hydride species undergo a reaction with CO leading finally to CH_3OH. In a pure oxide, the equilibrium concentration of $[V_0^{++}]$ is low, but in a contact with a metal a part of electrons is transferred from the vacancies on to the metal and by that a higher vacancy-concentration is stabilized at equilibrium. Frost predicts that Ag must do the same as Cu and makes an estimate of the equilibrium concentration of $[V_0^{++}]$, which estimate should show that the increase of the number of the stablized vacancies is realistic and sufficiently high to explain the higher rates of synthesis with Cu or Ag on various oxides, in comparison with metal free oxides.

1) The first doubt which rises is of qualitative character but not of a negligible weight. It is known that upon synthesis of CH_3OH, Cu is partially oxidized [3]. Then, according to Frost one has to believe that an oxygen vacancy [or Zn°] remains stable under the conditions that Cu° is oxidized. This does not seem very probable when the corresponding heats of formation are considered: that for ZnO is about twice as high as for Cu-oxides.

2) Frost [1] makes an estimate of the number of $[V_0^{++}]$, the active sites of methanol synthesis in his model. In this estimate M is used, the number of metal states available to receive electrons. Frost puts M equal to the number of metal atoms in direct contact with the oxide, which is encapsulating the metal particles. Since, he is considering (see p. 577) Cu particles of 0.7–1.5 nm, i.e. the metal is in a state of very high dispersion, almost all Cu atoms should bear a charge. However, such concentration of charge on small particles would make the particles unstable (an electrostatic explosion would be likely).

3) One reads on page 577: "strong vacancy segregation does not occur" and on page 578 one finds an assumption that "vacancies are concentrated at the

surface of the thin oxide overlayers" (i.e. layers of 0.5–5 nm thickness, encapsulating Cu particles). If the assumption concerning segregation is removed the surface concentration of $[V_0^{++}]$ would be lower. Also the value taken for the bulk concentration of oxygen vacancies is rather high. Together with point 2) this would all bring the surface concentration of active sites from the estimated 10^{12}–10^{13} cm^{-2} down by at least 1 or 2 orders of magnitude.

4) Palladium on MgO has a reasonably high activity in methanol synthesis, but how many $[V_0^{++}]$ can be expected in MgO?

5) Copper prepared from acidic precursors on very pure silica is completely inactive in methanol synthesis [4], but Cu from precursors which corrode SiO_2 and which thus enable formation of Cu^+, Cu^{++} silicates. is active [5]. It seems thus more likely that stabilisation of Cu-ions and not stabilisation of $[V_0^{++}]$ in SiO_2 is the way by which active sites are created.

6) A very recent investigation of the AG/CeO_2 system [6] revealed that silver is not active in the synthesis and functions rather as a poison. An earlier paper [7] showed that with Pd catalysts, Ag was a poison too. Thus, a question rises whether the Ag/ThO_2 catalysts used by Frost were not unintentionally promoted by incidental contaminations like Pd, often present in commercial Ag, or by Fe, a possible contaminant of ThO_2 or CO gas (carbonyl). Additional information on the purity of chemicals used would be very helpful.

References

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V. Ponec

Gorleus Laboratories,
Leiden University,
P.O. Box 9502,
2300 RA Leiden
The Netherlands