

## LETTER TO THE EDITOR

### Response to "Comment by Sadykov and Tikhov"

In their comment, Sadykov and Tikhov point out that for copper and copper oxide catalysts that have a substantial amount of bulk phase, the defect structure of the solid influences the catalytic properties.

In our recent studies to elucidate the effect of the oxidation state of copper on its kinetics of carbon monoxide catalytic oxidation, we avoided this problem. We utilized evaporated copper thin films of a few monolayers thickness (less than 10 ML) deposited on graphite. When we oxidized these samples at various oxygen partial pressures or reduced the copper oxide thin films, equilibria of stoichiometry and oxidation states between the surface and the few bulk layers of copper were achieved in minutes at 300° or at lower temperatures. This was readily verified by X-ray photoelectron and auger electron spectroscopies. Thus the catalytic effects due to the presence of bulk defects in three-dimensional copper or copper-oxide phases that do not equilibrate readily with the surface composition and structure were totally absent in our studies.

The comments by Sadykov and Tikhov point to one of the main reasons for irreproducibility in catalytic studies of oxidation reactions over metals or oxidized metals. In the presence of a substantial amount of bulk phase of the

catalyst or catalyst precursor, the surface composition and oxidation state of the surface atoms are often controlled by the slow bulk diffusion of metal ions, oxygen vacancies, and oxygen atoms. This makes the activity of the catalyst dependent on the solid-state chemistry of the bulk phase that can be the source of irreproducibility of results from laboratory to laboratory.

We recommend that, at least for model studies, thin layers of catalysts with negligible bulk phase should be used to facilitate the establishment of surface-bulk equilibrium during pretreatment or during the first few minutes of the catalytic oxidation reaction.

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