Revealing Hydrogen Spillover Pathways in Reducible Metal Oxide Supports

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Hydrogen spillover is a dynamic phenomenon which is initiated by the dissociation of hydrogen molecules followed by the migration onto the reducible metal oxide supports.¹ Spilled hydrogen atom shows specific behavior compared with gaseous hydrogen, thus it dramatically promotes the reduction of metal ions and the catalytic performance. However, in-depth understanding of its dynamic behavior, such as at what temperature it can take place, what pathway it follows, and the region to where hydrogen migrates, is still poorly understood because the observation method is not well established.

Our group has succeeded in the synthesis of binary alloy NPs catalysts with essentially immiscible metal combinations (Ru-Ni and Rh-Cu) on a TiO₂ support by utilizing spilled hydrogen atoms as a strong reductant. On the other hand, non-reducible γ -Al₂O₃ and MgO supports, whose hydrogen spillover abilities are inferior to that of TiO₂, afforded segregated NPs under the identical synthetic conditions.²⁻³ This means that the formation of non-equilibrium alloys strongly reflects the hydrogen spillover ability of the support surface.

In this work, we evaluated hydrogen spillover pathways in typical reducible metal oxide supports such as TiO_2 , CeO_2 and WO_3 by combining the specific formation of non-equilibrium Ru-Ni alloy nanoparticle, *in-situ* techniques, kinetic analysis, and density functional theory calculation. The combined experiments revealed that TiO_2 and CeO_2 allowed the preferential migration of dissociated hydrogen atoms over their surfaces, whereas hydrogen atoms preferably migrated within the bulk over WO_3 .⁴



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