

Oxide catalysts improved by local modifications: methane and CO₂ activation

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We are interested in improving the catalytic activity of oxides for methane or CO₂ activation and conversion to high value chemicals. This can be done by cation doping (i.e. replace the cation of the oxide with another cation: for example, to form Pt_xCe_{1-x}O₂), anion doping (i.e. replacing the oxygen atoms on the oxide surface with another anion, for example to form La₂O_{3-x}Cl_{2x}), or by adsorbing molecule sized oxide clusters on an oxide surface (for example, to form VO_x/TiO₂). For lack of time we limit this presentation to cation doping. We used density functional calculations to determine the properties of the doped oxides and the mechanisms through which they interact with various reactants. In particular we examine which dopant-oxide pairs lead to the formation of active oxygen atoms on the surface, or activate gas-phase oxygen by adsorption on the dopant, or activate dissociative adsorption of methane. We have shown by calculations and experiments that Ti doped ZnO will adsorb gas phase oxygen molecules, weaken the O-O bond and turn the adsorbed O₂ into a good oxidant. Experiments and calculations show that Pt doped ceria is more active for methane oxidation and dry reforming than either ceria or metallic Pt supported on ceria.