Methane Activation on α-Fe_2O_3: A DFT Study

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Anthropogenic greenhouse gas emissions are a growing concern due to the exponential increase in energy demand and their associated environmental impact. Methanol and formic acid are a few examples of liquid oxygenates derived from methane that benefit the environment by reducing CO_2 emissions [1]. The activation of methane is a crucial step towards the synthesis of valuable oxygenates [2]. However, these products may oxidize and produce carbon dioxide. Some studies suggest that FeIV boosts methane activation and that certain transition metals prevent further overoxidation [3-5].

We aim to investigate how different iron species (FeIII and FeIV) enhance or hinder the activation of methane on α-Fe_2O_3, and how copper influences the kinetic rates of carbon dioxide formation from formate by comparing α-Fe_2O_3 with $CuFe_2O_4$, using spin-polarized density functional theory (DFT) calculations. FeIV=O species are highly active in methane dehydrogenation compared to FeIII species. We predict that methane and an oxidizing agent such as hydrogen peroxide can react with the surface, and lead to the formation of CH_3*, OOH* and CH_3OOH* intermediates with relatively low barriers. CH_3OOH* is decomposed to CH_3OH and H_2O by reacting with 2H* adsorbed on the surface [6].

We show copper inhibits the overoxidation of formate to CO_2 by comparing α-Fe_2O_3 with $CuFe_2O_4$. Relative barriers of formate decomposition are higher in Cu-containing surfaces preventing the formation of CO_2. We find both copper and FeIV=O sites and are crucial for the synthesis of methanol and formate from methane oxidation reaction.

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