

# Computational studies of nickel catalysed reactions relevant for hydrocarbon gasification

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# Abstract

Sustainable energy sources are of great importance, and will become even more important in the future. Gasification of biomass is an important process for utilization of biomass, as a renewable energy carrier, to produce fuels and chemicals. Density functional theory (DFT) calculations were used to investigate i) the effect of co-adsorption of water and CO on the Ni(111) catalysed water splitting reaction, ii) water adsorption and dissociation on Ni(111), Ni(100) and Ni(110) surfaces, as well as iii) formyl oxidation and dissociation, iv) hydrocarbon combustion and synthesis, and v) the water gas shift (WGS) reaction on these surfaces.

The results show that the structures of an adsorbed water molecule and its splitting transition state are significantly changed by co-adsorption of a CO molecule on the Ni(111) surface. This leads to less exothermic reaction energy and larger activation barrier in the presence of CO which means that far fewer water molecules will dissociate in the presence of CO.

For the adsorption and dissociation of water on different Ni surfaces, the binding energies for H<sub>2</sub>O and OH decrease in the order Ni(110) > Ni(100) > Ni(111), and the binding energies for O and H atoms decrease in the order Ni(100) > Ni(111) > Ni(110). In total, the complete water dissociation reaction rate decreases in the order Ni(110) > Ni(100) > Ni(111).

The reaction rates for both formyl dissociation to CH + O and to CO + H decrease in the order Ni(110) > Ni(111) > Ni(100). However, the dissociation to CO + H is kinetically favoured. The oxidation of formyl has the lowest activation energy on the Ni(111) surface.

For combustion and synthesis of hydrocarbons, the Ni(110) surface shows a better catalytic activity for hydrocarbon combustion compared to the other surfaces. Calculations show that Ni is a better catalyst for the combustion reaction compared to the hydrocarbon synthesis, where the reaction rate constants are small.

It was found that the WGS reaction occurs mainly via the direct pathway with the  $\text{CO} + \text{O} \rightarrow \text{CO}_2$  reaction as the rate limiting step on all three surfaces. The activation barrier obtained for this rate limiting step decreases in the order Ni(110) > Ni(111) > Ni(100). Thus, the WGS reaction is fastest on the Ni(100) surface if O species are present on the surfaces. However, the barrier for desorption of water (as the source of the O species) is lower than its dissociation reaction on the Ni(111) and Ni(100) surfaces, but not on the Ni(110) surface. Therefore the direct pathway on the Ni(110) surface will dominate and will be the rate limiting step at low H<sub>2</sub>O(g) pressures. The calculations also reveal that the WGS reaction does not primarily occur via the formate pathway, since this species is a stable intermediate on all surfaces.

All reactions studied in this work support the Brønsted-Evans-Polanyi (BEP) principles.

**Keywords:** DFT, H<sub>2</sub>O, CO, adsorption, dissociation, formyl, hydrocarbon combustion, hydrocarbon synthesis, water gas shift, gasification, Ni(111), Ni(110) and Ni(100)