First principles reaction path analysis of the Fischer-Tropsch initiation and chain growth mechanism

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Introduction

Fischer-Tropsch synthesis (FTS) is rapidly regaining interest as a process for the conversion of synthesis gas (CO/H_2) to liquid fuels. CO dissociation is generally proposed to be the rate limiting step [1], and is followed by hydrogenation and C-C coupling to yield long chain hydrocarbons. Different mechanisms have been proposed for C-C coupling [2]. CH_2 polymerization following the carbide mechanism is the oldest suggestion. Dimerization between the hydroxyl methylene intermediates was proposed by Anderson and Emmett, while Pichler and Schulz more recently suggested CO insertion into adsorbed alkyl intermediates as the dominant C-C coupling mechanism.

To gain a molecular level understanding of the mechanism, various possible initiation and chain growth mechanisms were studied for a Co catalyst using density functional theory. Such mechanistic understanding might allow to begin to design more active FTS catalysts or allow controlling the selectivity towards specific hydrocarbon products.

Results and Discussion

Though CO dissociation has been proposed as the initiation step for FTS, the calculated dissociation barrier on a Co(0001) surface is 220 kJ/mol, consistent with literature values [1]. This high value does not seem consistent with measured turnover frequencies at typical FTS conditions of 200 to 240 °C. Though step sites lower this barrier to 195 kJ/mol, an alternative CO activation mechanism might be involved. Recent DFT studies on Ru(0001) suggest that a faster CO activation pathway might exist through the formation of CHO and CH_2O species which dissociate to O and CH and CH_2 intermediates, respectively, which then undergo C-C coupling [3]. Also on Co(0001), this mechanism opens up a faster pathway to CO activation and the calculated activation barriers for this pathway are significantly lower than for the CO dissociation pathway (Figure 1). A similar mechanism was recently proposed by Inderwildi et al. [4].

The CH_2 intermediates formed in the CO activation step can next undergo C-C coupling to form long chain hydrocarbons. The barrier for this reaction, 67 kJ/mol (Table 1), is fairly low. However, alternative C-C coupling and CO activation mechanisms can be proposed. Experimental results from Blyholder and Emmett using radio-labeled ketene suggest that CO can participate in chain growth [6], similar to the CO insertion mechanism proposed by Pichler and Schultz. Experimental studies under commercial FTS conditions over iron catalysts provided additional support for the CO insertion mechanism [2].

Table 1 summarizes calculated barriers for CO insertion in various alkyl species on a Co(0001) surface. Coupling between CH_2 and CO has a low barrier of 55 kJ/mol, and could be kinetically important, while coupling between CH_3 and CO is significantly more difficult. To close the catalytic cycle, additional reactions were investigated. Important steps are the hydrogenation of the CH_xCO species to CH_xCHO, followed by C - O scission to close the cycle. Selected barriers are summarized in Table 1, and indicate that a path via CH_2CHO is likely. Further calculations will allow comparing other possible reaction pathways. Coupling between R-CH and CO continues the catalytic cycle. A barrier of 72 kJ/mol was calculated for CH3CH coupling to CO. In addition, the CO insertion might provide an explanation for the formation of a small fraction of oxygenates during FTS.

Conclusion

First principles reaction path analysis was used to investigate the mechanism of FTS on a Co(0001) surface. DFT calculations indicate that hydrogen mediated CO activation might provide a faster initiation pathway than CO dissociation. In addition to CH_2 - CH_2 coupling, CO insertion might offer a competitive pathway to form long chain hydrocarbons. A succession of CO to alkyl coupling, hydrogenation, and C-O bond activation steps is proposed based on DFT calculations. Further microkinetic simulations will allow quantifying the importance of the different pathways under different conditions.

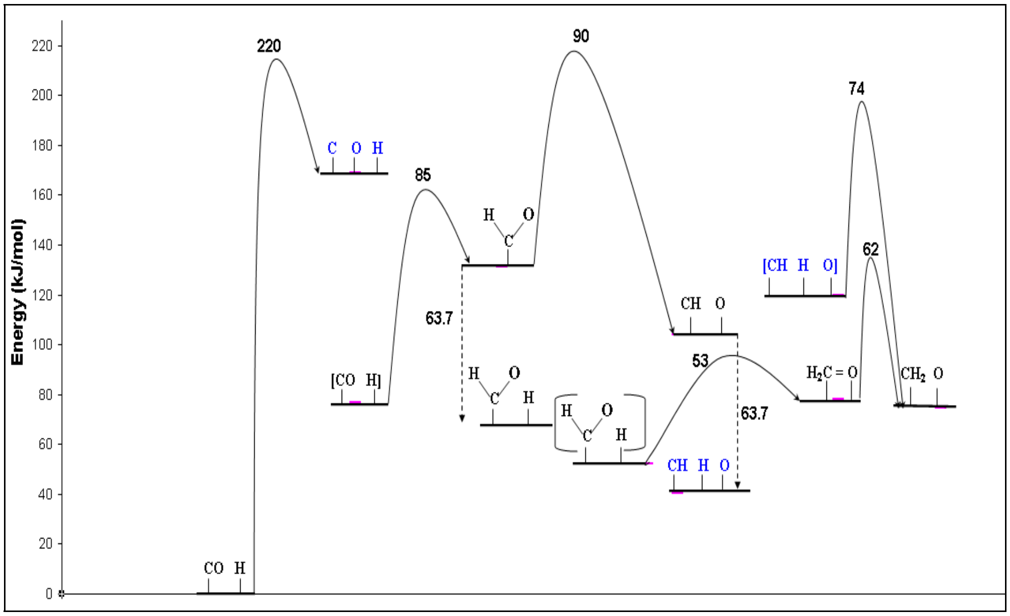

Figure 1. Activation energies for CO activation and formation of CH_x species on Co(0001) surface

Table 1. Activation energies, E_a for selected species on Co(0001) surface

Reaction	**E_a (kJ/mol)**	**ΔH (kJ/mol)**
$CH + CO \rightarrow CHCO$	99	62
$CH_2 + CO \rightarrow CH_2CO$	***55***	***40***
$CH_3 + CO \rightarrow CH_3CO$	130	14
$CHCHO \rightarrow CHCH + O$	26	-78
$CH_2 + CH_2^*$	67	N/A

Note: * from reference [5]

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