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A New Insight into Fischer−Tropsch Synthesis

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As the global reserves of oil are being consumed, Fischer−Tropsch (FT) synthesis that converts CO and H_2 to high-molecular-weight hydrocarbons becomes a more and more important route for the production of fuels and chemicals.[1a] Despite tremendous efforts devoted to this process[l−9] in the last 70 years, the reaction mechanism of FT synthesis remains uncertain. With extensive density functional theory (DFT) studies on FT reactions, we obtain relative stabilities of many key intermediates and compare quantitatively several C/C coupling mechanisms that are likely to be involved. We found that a well-regarded $CH_2 + CH_2R$ (R = H or alkyl) mechanism[2] possesses high reaction barriers, and a stepwise C + CR mechanism has been identified that may be relevant to FT synthesis.

It is generally believed that the first step of the FT synthesis is the CO and H_2 dissociations followed by hydrogenation processes ($C + H \rightarrow CH$, $CH + H \rightarrow CH_2$, $CH_2 + H \rightarrow CH_3$). Then the CH_x species ($x = 0, 1, 2$) couple with each other (C/C coupling) to form higher-weight hydrocarbons.[1−9] Among all the steps, the C/C coupling is the key step,[la] which competes with the CH_x hydrogenation reactions. Since the discovery of FT synthesis in 1926, the C/C coupling has been extensively studied, and many elegant experimental works have been carried out[2a,b,7] (see a recent review on FT synthesis in ref la and the references therein). Perhaps the best-regarded mechanism proposed is the $CH_2 + CH_2R$ mechanism,[la,2a,2b] which can be described as follows: $CH_2 + CH_3 \rightarrow CH_2CH_3$; $CH_2 + CH_2R \rightarrow CH_2CH_2R$. However, little quantification on individual elementary steps has been carried out. Aiming to provide insight into FT synthesis, we have systematically studied some key reactions using density functional theory.

Total energy calculations using DFT-slab approach with a GGA functional[11a] and plane wave basis set were performed.[12] The Ru metal that possesses the highest FT reactivity was selected;[1,3] both flat and stepped Ru(0001) were studied to shed light on surface structural effects. The prototypical C/C coupling reactions through many possibilities, that is, C + C, C + CH, $C + CH_2$, CH + CH, $CH + CH_2$, $CH_2 + CH_2$, and $CH_2 + CH_3$[10] were investigated together with some related hydrogenation reactions in FT synthesis. The accuracy of the current DFT-slab approach, in particular for calculating the activation energies (the zero-point energy is not included) in heterogeneous catalysis, has been demonstrated.[14−19]

We first determined the most stable initial state (IS) for the chemisorbed CH_x species ($x = 0, 1, 2, 3$) on the Ru(0001), terrace, and step-edge of stepped surfaces. Then transition states (TSs) for the C/C coupling reactions between these chemisorbed CH_x were searched. The barriers (E) for each reaction were calculated, which are listed in Table 1. It shows three interesting features: (i) Ru is indeed very active for FT synthesis, agreeing with the well-known fact as mentioned above.[1,20] The lowest barrier for the C/C couplings is only 0.43 eV on Ru (the C + CH reaction on Ru-steps). (ii) *Steps* are generally more active than flat surfaces. This is consistent with recent experimental work, which suggested that defects are the active sites for FT synthesis on Co-based catalysts.[9] (iii) It is the *C + CH reaction* that possesses the lowest barrier (only 0.43 eV) on Ru-steps among all the C/C coupling reactions, while the E_a of $CH_2 + CH_3$ (the first step in the $CH_2 + CH_2R$ mechanism) is enormous on both the flat and stepped surfaces.

Table 1. Calculated Reaction Barriers (E_a) for C/C Couplings on Ru Surfaces

	Ru-step	Ru(0001)		Ru-step	Ru(0001)
C + C	1.05	1.51	$CH + CH_2$	1.20	0.97
C + CH	**0.43**	1.01	$CH_2 + CH_2$	0.59	1.23
$C + CH_2$	0.56	1.08	$CH_2 + CH_3$	1.40	1.80
CH + CH	0.95	0.87			

[a] The unit of E_a is eV

Figure 1 in Supporting Information highlights the IS, TS, and final state (FS) of the C + CH reaction on monatomic stepped Ru. Because the C + CH is the reaction with the lowest barrier among all the C/C couplings and can be considered as a prototypical reaction for C + CR, the chain growth in FT synthesis may be expected to follow a C + CR pattern. To further confirm its feasibility, we also calculated the $C + CCH_3$ reaction on the same monatomic Ru step. The E_a for the formation of $CCCH_3$ is 0.62 eV, which is still quite low.

To complete the microscopic picture and to obtain an overall energetic diagram for FT synthesis, we also studied hydrogenation reactions in the chain growth, that is, $CCH + H \rightarrow CCH_2$ and $CCH_2 + H \rightarrow CCH_3$, and a side-reaction, namely CH_4 formation.[21a] Their reaction pathway and reaction barriers were calculated, which results in an overall reaction energy diagram shown in Figure 1, combining with the C/C couplings discussed above. Figure 1 shows three distinct reaction routes. Route 1 leads to CH_4, which can be considered as the side reaction in FT synthesis. Both routes 2 and route 3 result in chain growth. In route 2, the chain grows with a C + CR pattern. The details of this route are illustrated in Figure 2 and described in the figure caption. Route 3 represents the $CH_2 + CH_2R$ mechanism, in which the chain grows by repeating the reaction of $CH_2 + CH_2R \rightarrow CH_2CH_2R$. A careful examination of Figure 1 reveals the following interesting features. First, CH is the most stable C1 species on Ru, while CH_2 is kinetically unstable due to its tiny barrier (0.17 eV) to decompose into CH.[21a] This is consistent with the experiments that the populations of C and CH (or CR) are always much higher than that of CH_2 (or CHR) on catalysts under FT conditions.[3] An early experimental work also found that CH_2 dehydrogenation on a Co surface occurs at a very low temperature of 180 K.[23] Second, in route 2 the reaction intermediates, that is, C, CH, CCH, CCH_2, CCH_3 are thermodynamically more stable than the intermediates in other routes. More importantly, the C/C coupling barrier in route 2 (0.43 eV for C + CH, and 0.62 eV for $C + CCH_3$) is lower than that in CH_4 formation

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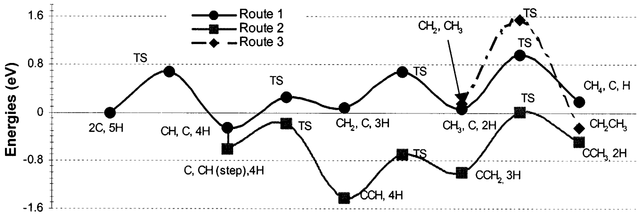

Figure 1. Overall energy diagram in FT synthesis. Route 1: CH_4 formation on flat Ru(0001). Route 2: C + CR mechanism (see Figure 2) on Ru-steps (Table 1). Route 3: $CH_2 + CH_2R$ mechanism (all the steps (i.e., CH, CH_2, and CH_3 formation) are the same with route 1 except the last step, $CH_2 + CH_3$, which was calculated on Ru-steps (Table 1)). The energy of each state is referred to the initial state, i.e., two C (hcp hollow site) and five H atoms (fcc hollow site) adsorbed on Ru(0001) (assuming no interaction between all adsorbed species). The discontinuity of the first point in route 2 from route 1 is due to the fact that C and CH are more stable on Ru-steps.

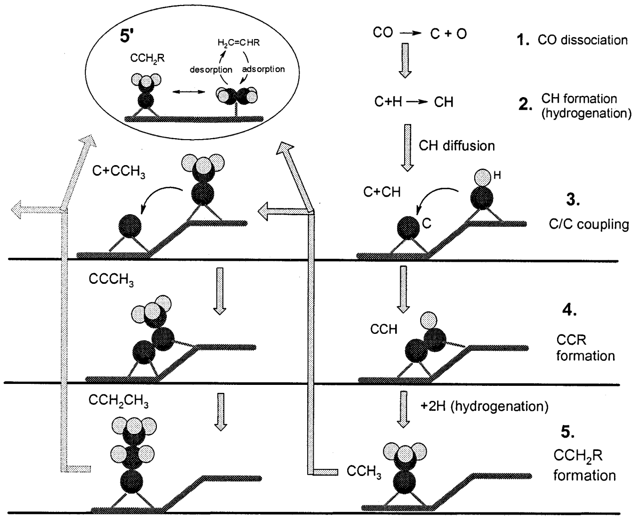

Figure 2. C + CR mechanism for Fischer−Tropsch synthesis based on our results. (1) CO and H_2 dissociation. (2) C + H → CH reaction and CH diffuses to a step site. (3) At steps C + CH → CCH. (4) CCH formation. (5) CCH + H → CCH_2 and CCH_2 + H → CCH_3. CCH_3 then diffuses to another step to start C + CCH_3 → $CCCH_3$. Alternatively, CCH_3 may rearrange to ethylene, C_2H_4, which desorbs readily from the surface (5′).

(0.90 eV in the CH_3 + H step). Once the C−C bond is formed, the possibility of C−C bond breaking is very small due to its high barrier (CCH → C + CH, E_a = 1.26 eV). This is consistent with the experimental fact that the formation of long-chain hydrocarbons is favored over CH_4 on Ru under FT conditions. Third, route 3, the well-regarded $CH_2 + CH_2R$ mechanism, is the worst one energetically, and it may not occur under normal FT conditions: (i) CH_2 that is required as a building block in route 3 is kinetically unstable and its population is very low, as mentioned, and (ii) the barrier of the key C/C coupling step in route 3 ($CH_2 + CH_3$) is far too high (1.40 eV on steps and 1.80 eV on a flat surface) for this reaction to occur. Consider that the population of H atoms on the surface is much higher than CH_2 and an enormous barrier difference exists between H + CH_3 (E_a = 0.90 eV) and $CH_2 + CH_3$ (E_a = 1.40 eV), our results indicate that route 3 can never compete with CH_4 formation. Even a CH_2CH_3 is formed (through other routes); it is expected that the next step, $CH_2 + CH_2CH_3$, is still hindered by a high barrier because the reacting C (in $CH_2{-}CH_3$) is chemically similar to the C in CH_3. Maitllis et al.[7b] have indeed demonstrated that alkyl species (e.g., CH_2CH_3) are not the reaction intermediates in the C/C coupling: The addition of ^{13}C-labeled ethyl (generated from CH_2CH_3Br) is not observed in the final FT products.

It is worth mentioning a well-known experimental work in FT synthesis: Brady and Pettit[2a] found that the addition of CH_2N_2 into syn-gas would incorporate the C from CH_2N_2 into the FT products. This observation was used to support the $CH_2 + CH_2R$ mechanism because CH_2N_2 can readily produce CH_2. However, this result does not contradict our calculations. First, CH_2 (from CH_2N_2) may well decompose into CH, which then participates in the chain growth. Second, our calculations suggest that the CH_2 may directly react with C (CH_2 + C, E_a = 0.56 eV) or couple with each other ($CH_2 + CH_2$, E_a = 0.59 eV) if they have not decomposed. Nevertheless, our calculations indicate that the C + CR is favored pathway under normal FT conditions (CO and H_2 as reactants on Ru).

Supporting Information Available: S-Figure 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Ultrasoft pseudopotentials were used to describe the ionic cores.[11b] The vacuum region between slabs was 10 Å, and a cutoff energy of 340 eV was used. To fully compare the reactivity of the same reaction on flat and stepped surfaces, large unit cells, $p(4 \times 2)$ or $p(4 \times 3)$ with four layers, were used to model the flat Ru(0001) surfaces. The same unit cells with two rows in the first layer being removed were utilized to model the monatomic stepped surfaces.[13] The obtained step-II (S-Figure 1; also see ref 13) that is known to be more reactive is used to investigate C/C coupling reactions. All the atoms of the surface were fixed at their bulk-truncated positions. The surface relaxation was checked, and its effect on the reaction barrier concerned was found to be about be 0.1 eV. The surface Brillouin zone was sampled by $2 \times 3 \times 1$ *k*-points for $p(4 \times 2)$ unit cell and $2 \times 2 \times 1$ *k*-points for $p(4 \times 3)$ unit cell. Convergence with respect to *k*-point sampling was checked by increasing *k*-point sampling up to $3 \times 4 \times 1$, and the difference between *k*-point samplings was found to be small (<0.05 eV). Transition states (TSs) of reactions were searched using a constrained minimization technique.[14−18]
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(21) (a) Our calculated results are in good agreement with the previous work on methane activation (Ciobica, I. M.; Frechard, F.; van Santen, R. A.; Kleyn, A. W.; Hafner, J. *J. Phys. Chem. B* **2000**, *104*, 3364). (b) Using EH and ASED methods van Santen et al. (van Santen, R, A.; de Koster, A.; Koerts, T. *Catal. Lett.* **1990**, *7*, 1) showed that CH + CH_x and $CH_2 + CH_x$ pairs repel each other under tested conditions, while C + CH_x reactions have lower barriers (1−2 eV).
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