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Biofuels

Mechanistic Studies of Hydrocarbon Combustion and Synthesis on Noble Metals**

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Climate change is arguably the most severe threat currently faced by mankind.[1] The main reason for amplification of the changing climate is the emission of greenhouse gases, mainly CO_2, and the main emission source is the combustion of fossil fuels.[2,3] It is therefore of paramount importance to move to a carbon-neutral fuel economy, and one route towards such an economy may be the conversion of biomass into liquid fuels (i.e. liquid hydrocarbons).[4] Biomass, which is generated from CO_2 and H_2O by photosynthesis, can thus be converted into liquid fuels that are again combusted to H_2O and CO_2. In this scheme, energy is ultimately extracted from sunlight, through a short-period carbon cycle, without release of carbon from fossil fuel reserves into the atmosphere. Three of the six steps in the carbon cycle depicted in Figure 1 are carried out utilizing heterogeneous catalysis (1–3). In the event that all the steps are feasible, the depicted cycle would be a possibility to provide energy in portable form (e.g. for individual transportation) without significantly increasing the amount of greenhouse gas in the atmosphere.

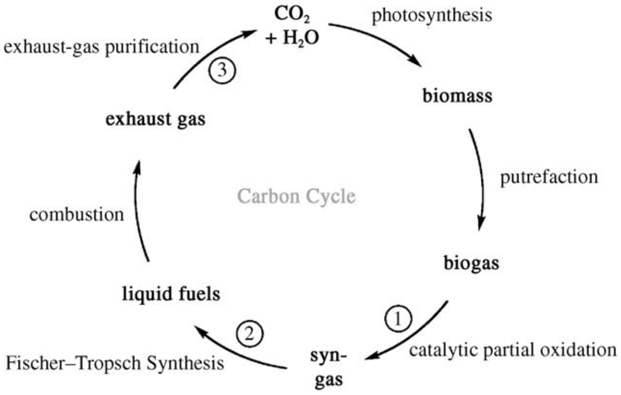

Figure 1. Carbon cycle, the catalytic steps are numbered 1–3.

To improve the catalytic processes in the cycle and advance towards a feasible carbon-neutral economy, the mechanisms enabled by the catalysts, mainly on the surface of an active component, have to be fully understood. Very recently, it has been suggested that many previously proposed reaction mechanisms on transition-metal surfaces are outdated and that alternative pathways must now be considered.[5–10] Various recent publications suggest that oxidation of hydrocarbons is not a simple dissociation of the hydrocarbon into adsorbed carbon and hydrogen followed by oxidation reactions,[11,12] as assumed in many previous studies; direct reaction of CH fragments with adsorbed oxygen can sometimes be the most likely pathway.[5] In these pathways an oxymethylidyne (CHO, formyl) species is formed, which dissociates to yield adsorbed hydrogen and CO. Interestingly, it seems that reaction via this CHO species is also the main reaction pathway in the synthesis of hydrocarbons over certain catalysts, contrary to previous assumptions.[6,10] Herein, we present novel mechanistic pathways of both processes—the combustion and the synthesis of hydrocarbons—on various metals which highlight and develop this new understanding. We will draw parallels between different metals and reactions and point out why this new understanding is of the utmost importance for the comprehension and consequently for the steering of heterogeneously catalyzed reactions. Descriptions of the DFT procedures can be found elsewhere,[6] although we note that spin effects were here included only in the case of the ferromagnetic cobalt surface.

Catalytic combustion of hydrocarbons (steps 1 and 3 in the carbon cycle): We previously showed that in the oxidation of hydrocarbons on Rh{111}, the main reaction pathway is that methylidyne (CH) is formed by hydrocarbon dissociation and that this species is oxidized to CHO and subsequently dissociates to $CO_{(s)}$ and $H_{(s)}$.[5] Dissociation of $CH_{(s)}$ into its components prior to oxidation can be neglected according to our DFT-based microkinetic simulations. To evaluate if this state of affairs is generally true, we studied the analogous reaction pathway on two other “classic” oxidation catalysts, Pt and Pd, in the present study and compared it to the direct dissociation of $CH_{(s)}$ (Table 1. It seems that for Pt{111} CH dissociation and oxidation are kinetically competitive, while oxidation to $CHO_{(s)}$ is thermochemically favored. The much more interesting result, however, is the very low barrier found for the oxidation of $CH_{(s)}$ on Pd{111}.

Whilst it is known that Pd is the most active catalyst for the low-temperature oxidation of methane, the nature of the active site is not fully clear and remains the topic of much debate.[13,14] Bell and co-workers presented results strongly suggesting that the active sites for low-temperature combus-

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Table 1: Energetics of the hydrocarbon combustion and formation by means of full dissociation or direct reaction.[a]

	Catalytic hydrocarbon combustion					
	$CH_{(s)} \rightarrow C_{(s)} + H_{(s)}$		$CH_{(s)} + O_{(s)} \rightarrow CHO_{(s)}$		$CHO_{(s)} \rightarrow CO_{(s)} + H_{(s)}$	
	E_a	ΔE	E_a	ΔE	E_a	ΔE
Pt{111}	1.12	+0.59	1.12	−1.18	0.57	−0.89
Rh{111}[5]	1.28	+0.67	1.15	−0.14	0.30	−1.33
Pd{111}	1.65	+0.72	0.78	−1.38	0.36	−1.16
Ni{111}[9]	1.37	+1.21	0.80	−0.51	0.29	−1.18

	Catalytic hydrocarbon synthesis					
	$CO_{(s)} \rightarrow C_{(s)} + O_{(s)}$		$CO_{(s)} + H_{(s)} \rightarrow CHO_{(s)}$		$CHO_{(s)} \rightarrow CH_{(s)} + O_{(s)}$	
	E_a	ΔE	E_a	ΔE	E_a	ΔE
Co{0001}[6]	2.82	+2.09	1.31	+1.00	1.00	+0.22
Ru{0001}	2.23	+0.68	0.99	+0.97	0.76	−0.85
Fe{111}[8]	1.76	−0.38	0.99	+0.57	1.17	−0.82

[a] Energies are derived from PW91 calculations, except those taken from Refs. [8,9], which are derived from PBE calculations. $E_a =$ activation energy, $\Delta E =$ reaction enthalpy. Results for Co, Fe, and Rh are taken from the literature; results for Ru, Pd, and Pt are part of the present study.

tion on a supported Pd catalyst are actually metallic Pd patches embedded in PdO.[13] The metallic Pd serves to dissociate methane more effectively than PdO, while oxygen is able to adsorb on the oxide. This—in combination with the low barrier for $CH_{(s)}$ oxidation—could potentially explain the low-temperature activity of Pd-based catalysts: oxygen adsorbs on PdO and by means of spillover this oxygen migrates to the metallic Pd patches. On these patches the oxygen originating from spillover is able to oxidize the CH fragment rapidly ($E_a = 0.78$ eV). Alternatively, Baiker and co-workers proposed a redox mechanism for the oxidation of CH_4 on Pd/PdO, in which PdO is reduced to Pd during the CH_4 oxidation.[14] In this case the pathway proposed herein would take place at the Pd/PdO interface.

If one considers only the CH-dissociation pathway, it would not be clear why metallic Pd should be particularly active in the low-temperature combustion of methane, since the activation barrier for this step is significantly higher on Pd than on either Rh or Pt (see Table 1). Taking the newly developed formyl pathway into account, however, banishes this seeming paradox: The reaction pathway via CHO is more favorable on all {111} surfaces studied, and in the case of Pd the barrier is lowest (0.78 eV) and the reaction is energetically most favorable (exothermicity of −1.38 eV). This, in combination with a constant oxygen supply by spillover from the surrounding oxide, is a compelling explanation for the low-temperature activity.[13] Spillover from PdO to metallic Pd is presently under investigation in our group. Additionally, we note that Freund and co-workers recently observed a $CHO_{(s)}$ species on Pd{111}[7] in the dehydrogenation of methanol using PM-IRRAS at millibar pressure and post-reaction XPS, indirectly bolstering our DFT results.

Such a CHO-mediated pathway was also recently described in the reforming of CO_2 to methane on Ni surfaces. Wang et al. investigated the conversion of $CH_{(s)}$ on Ni{111} and found that the barrier for dissociation is rather high (1.37 eV), while the barrier towards $CHO_{(s)}$ formation is almost 50 % lower (0.80 eV).[9] The dissociation of the $CHO_{(s)}$ species is activated by merely 0.29 eV, which clearly shows that CH dissociation is not the main reaction pathway.

Catalytic formation of hydrocarbons (step 2 in the carbon cycle): Interestingly, recent studies also indicate that $CHO_{(s)}$ species are an important reaction intermediate in hydrocarbon synthesis utilizing the Fischer–Tropsch process on Co surfaces.[6] For some time, the prevailing opinion has been that both CO and H_2 adsorb dissociatively on the Co surface, and that both C and O are subsequently hydrogenated yielding CH_2 and H_2O.[15] While H_2O desorbs, adsorbed CH_2 can undergo polymerization and hydrogenation reactions leading to alkane chains; this is the so-called "carbide" mechansim. Using DFT calculations and microkinetic simulations on Co{0001}, we recently demonstrated that the main reaction pathway is instead adsorption of CO and hydrogen, followed by two hydrogenation steps (forming CHO and thence CH_2O) and subsequent cleavage of the C–O bond, leading to $CH_{2(s)}$ and $O_{(s)}$ coadsorbed.[6] This process is energetically significantly more favorable than the carbide mechanism, and according to our simulations of the microkinetics under high pressure, this constitutes the exclusive reaction path.

To verify if this is also true for other metals applied as catalysts in the Fischer–Tropsch synthesis, we have now studied the carbide and the formyl pathways on Ru{0001} (Figure 2). Also in this case the formyl pathway is kinetically the more likely mechanism with barriers of 0.99 eV for the subsequent formation of $CHO_{(s)}$ and 0.76 eV for the formation of $CH_{(s)}$ and $O_{(s)}$, compared to a very high barrier towards CO dissociation of 2.23 eV. This strongly suggests that on this facet the reaction will definitely proceed by the formyl pathway rather than by the carbide mechanism. These findings hence further confirm that formyl formation and reaction should be included into kinetic modeling in order to produce accurate results.

In further justification of this statement, we note recent work by Ma et al., who carried out DFT calculations and determined an analogous stable CHO species on the kinked {111} facet of iron.[16] Subsequently Huo et al. carried out DFT calculations on the dissociation of CO and the formation of CHO on Fe{111}, and also this study came to the conclusion that a pathway via $CHO_{(s)}$ is kinetically favored over the carbide mechanism, since the dissociation barrier is considerably lower for the formyl pathway (1.17 eV vs. 1.53 eV).[8]

Similarly, Andersson et al. studied the methanation at Ni{111} surfaces using theoretical and experimental techniques and determined the dissociation barrier for CO to be 1.7–1.9 eV, while the adsorption energy is merely 1.2 eV.[10] These findings are in agreement with TPD experiments from the same group on CO-covered Ni, in which no CO

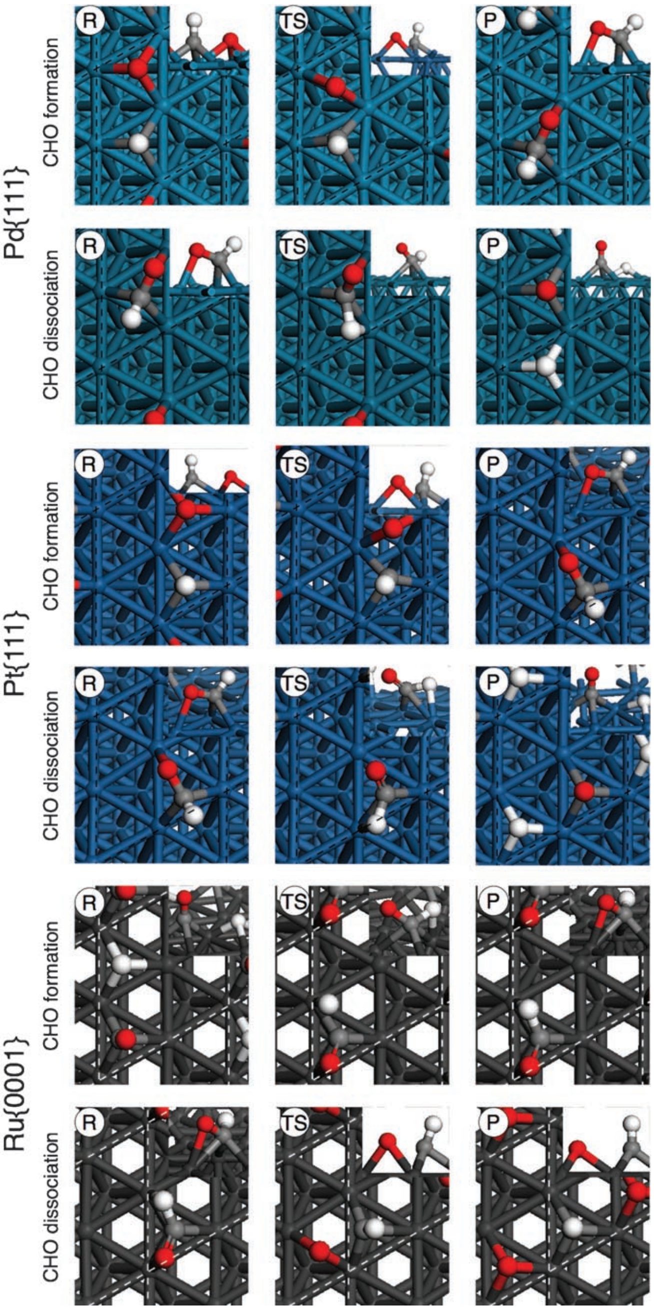

Figure 2. Reactant (R), transition state (TS), and product (P) structures for formyl formation and dissociation on Pd{111}, Pt{111}, and Ru{0001}. Side views are shown in the insets; C gray, O red, H white.

dissociation is observed. Reaction via a formyl species, however, involves activation barriers of 1.01 and 1.08 eV, that is, below the desorption energy. These independent findings additionally underline the central role played by formyl in the most recent mechanistic studies of catalytic hydrocarbon reactions.

Taken together, the experimental and theoretical studies discussed above clearly show a step-change in the development of mechanisms for reactions on surfaces: formyl now seems to be an essential intermediate species in both hydrocarbon combustion and synthesis. Most striking is that formation and combustion of hydrocarbons follow very similar routes in opposite directions, even though different metals are applied for the different processes (see Figure 2). Further comparison with previous results confirms this.[5,6,8–10] Such an observation, in combination with the paramount importance of heterogeneous catalysis for a carbon-neutral fuel economy, stresses the importance of first principles mechanistic research on metal surfaces. Recognition of the formyl pathways in catalytic hydrocarbon reactions, for instance, should change entirely the future interpretation of experimental work in this field.

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