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# Direct versus Hydrogen-Assisted CO Dissociation

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Carbon monoxide is a potential substitute for crude oil as a feedstock in the production of liquid hydrocarbons via the Fischer−Tropsch (F−T) process.[1] This process initiates through CO dissociation, and hence, a fundamental understanding of CO activation is of utmost importance. Extensive experimental and theoretical studies have been carried out to investigate the reaction path of CO dissociation and identify the active site that would be responsible for the low CO dissociation barrier.[2−11] These studies have confirmed that the active sites present along stepped and corrugated metal surfaces reduce the CO dissociation barrier. Basically, two mechanisms for CO activation have been hypothesized. One proposition suggests that chain growth in the F−T process is initiated via the carbide mechanism, which involves CO dissociation followed by hydrogenation to produce $CH_x$ species.

An alternative mechanism for CO dissociation that proceeds through hydrogen-assisted intermediates has also been proposed. Experimental work by Mitchell et al.[12] showed that the HCO and $H_2CO$ intermediates are formed from coadsorbed CO and H. Ciobica and van Santen[6] presented theoretical evidence that on the dense Ru(0001) surface, CO dissociation could also proceed through H insertion. Similarly, Inderwildi et al.[13] showed that on the dense Co(0001) surface, the formation of $CH_x$ species proceeds through the HCO and $H_2CO$ intermediates instead of the carbide mechanism. Morgan et al.[14] showed in an experimental and theoretical study that formation of the HCO intermediate on Ru(0001) and stepped Ru(109) surfaces is endothermic. In a combined experimental and theoretical work, Andersson et al.[15] proposed that CO dissociation on Ni surfaces proceeds via hydrogenated intermediates. These results suggest that on the dense surfaces, where the direct CO dissociation has a high barrier, hydrogen-assisted CO dissociation would be the favorable path. However, to our knowledge, the preferred pathway for CO dissociation on corrugated surfaces is not well-understood.

In the present work, we investigated the direct and H-assisted CO dissociation on a Ru(1121) surface. We propose that on this corrugated Ru surface, where the sixfold [fourfold (4F) + twofold or bridge (B)] active sites are responsible for low-barrier CO dissociation,[11] the carbide mechanism is the preferred path. We used the VASP code for the present study.[16] The computational details are given in the Supporting Information.

Let us first consider the direct CO dissociation path (i.e., the carbide mechanism). This path is shown in Figure 1. The CO molecule is situated at a stable sixfold site with C and O at 4F and B sites, respectively. This configuration is maintained for the complete dissociation path (Figure 1). Moreover, CO is preactivated ($r_{CO}$ =1.33 Å) in the adsorbed state, as C and O attain the stable 4F and B sites, respectively, and do not share metal atoms in the transition state. These factors lead to a low CO dissociation barrier of 65 kJ/mol (Figure 2). The reaction to form HCO from coadsorbed H and CO is shown in Figure 3a−c. The final state (FS) is shown in Figure 3c and corresponds to the HCO intermediate. The C moves out of the 4F site and has threefold (3F) coordination with the Ru surface. The hydrogenation barrier for forming HCO is 80 kJ/mol (Figure 2). This reaction is highly endothermic, with a reverse reaction barrier of only 5 kJ/mol. This is in agreement with earlier studies showing that HCO formation on corrugated Ru surfaces is difficult.[6,10,13] Moreover, Fan et al.[10] showed via experiments that the coadsorbed H displaces the precursor state of CO on the Ru(1121) surface, in agreement with our interpretation. Interestingly, the barrier for forming HCO is 15 kJ/mol higher than that for the direct dissociation path (Figure 2). Assuming that HCO may still be formed under nontrivial experimental conditions, we further studied CO dissociation from the HCO intermediate.

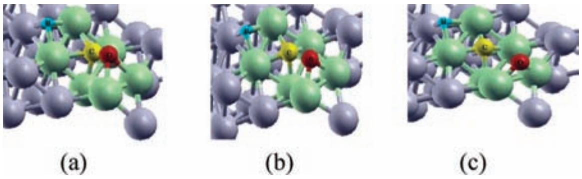

***Figure 1.*** (a) Initial-, (b) transition- and (c) final-state structures of the direct dissociation of CO from coadsorbed H and CO on the Ru(1121) surface. Gray, yellow, red, and blue spheres correspond to Ru, C, O, and H atoms, respectively. The sixfold active site for CO dissociation is highlighted in light-green.

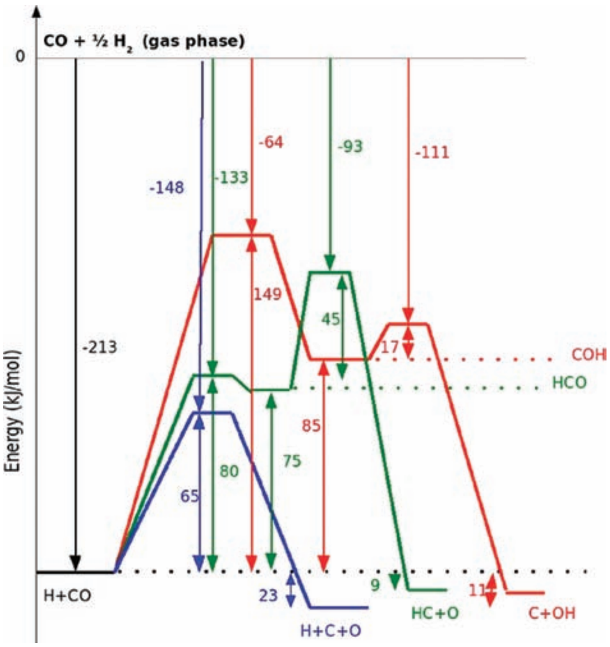

***Figure 2.*** Energetics of CO dissociation in the presence of coadsorbed H on the Ru(1121) surface. Blue line: direct CO dissociation. Green line: CO dissociation through the HCO intermediate. Red line: CO dissociation through the COH intermediate. The energies are given in kJ/mol with respect to gas-phase CO + $^1/_2H_2$.

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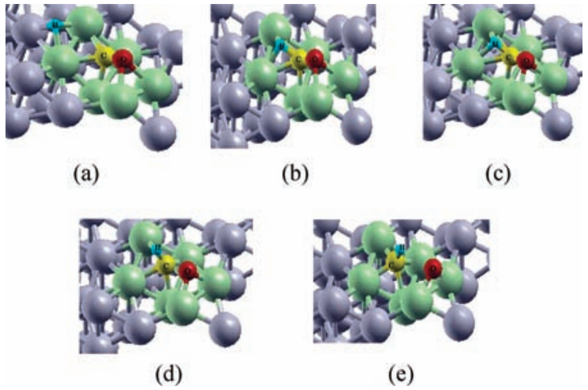

***Figure 3.*** CO dissociation path via the HCO intermediate on the Ru(1121) surface. Gray, yellow, red, and blue spheres correspond to Ru, C, O, and H atoms, respectively. The sixfold active site for CO dissociation is highlighted in light-green.

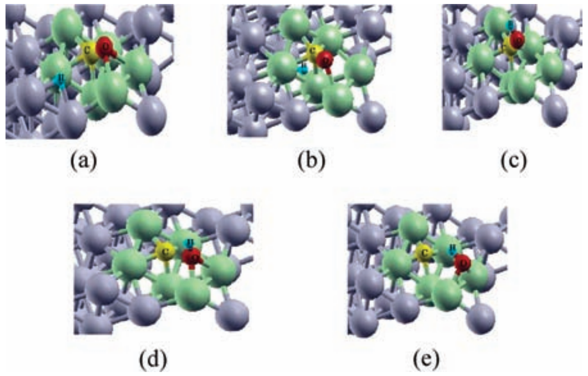

***Figure 4.*** CO dissociation path via the COH intermediate on the Ru(1121) surface. Gray, yellow, red, and blue spheres correspond to Ru, C, O, and H atoms, respectively. The sixfold active site for CO dissociation is highlighted in light-green.

The reaction to form CH and O from the HCO intermediate is shown in Figure 3c−e. The dissociation barrier is 45 kJ/mol, which is lower than the direct CO dissociation barrier (Figure 2). However, one should note that the overall barrier with respect to coadsorbed H and CO is 120 kJ/mol, which is much higher than that for direct CO dissociation (Figure 2).

The other alternative path we examined involves hydrogenation at the O end of CO to form the COH intermediate, as proposed for Ni surfaces by Andersson et al.[15] The reaction path is shown in Figure 4. The initial state again has H in the 3F site. The H atom in this 3F site (Figure 4a) is only 9 kJ/mol less stable than the one shown in the earlier initial state (IS) (Figure 1a). In the FS, the O atom moves out of the B site to form the OH bond (Figure 4c). The initial hydrogenation step to form the COH intermediate has a barrier of 149 kJ/mol (Figure 2) with respect to the most stable H site (Figure 1a). This high barrier can be attributed to moving the O atom from the stable B site during the hydrogenation. CO bond dissociation from the COH intermediate requires only 17 kJ/mol. This reaction path is shown in Figure 4c−e. One should note that to dissociate CO from the COH intermediate, one needs to overcome an overall barrier of 149 kJ/mol, which is 84 kJ/mol higher than the direct CO dissociation path (Figure 2). If we would ignore the initial hydrogenation steps in the formation of HCO and COH intermediates (Figure 2), then CO dissociation through the HCO and COH intermediates would require overall barriers of 120 and 102 kJ/mol, respectively. In this case, CO dissociation via the COH intermediate is more favorable than that via the HCO intermediate as a result of increased CO bond stretching in the COH intermediate ($r_{CO} = 1.42$ Å) relative to the HCO intermediate ($r_{CO} = 1.37$ Å). This is consistent with the results of Andersson et al.[15] for stepped Ni surfaces.

Our study clearly shows that the higher barrier required for the formation of hydrogenated intermediates relative to that for the direct CO dissociation path rules out the possibility that COH or HCO is the precursor state for CO dissociation on corrugated Ru surfaces.

In summary, our results demonstrate that direct CO dissociation on the corrugated Ru(1121) surface has a lower overall barrier than the hydrogen-assisted CO pathways. This is due to the highly endothermic steps to form the intermediates during the hydrogenation paths. Thus, the F−T mechanism on corrugated Ru surfaces consisting of sixfold active sites for CO dissociation proceeds through the carbide mechanism rather than the hydrogenated intermediates. Furthermore, we propose from the present study that the carbide mechanism will be the preferred path in the F−T process on stepped, double-stepped, and open surfaces and also on nanoparticles where active sixfold sites for CO dissociation can exist.

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**Supporting Information Available:** Model and computational details used in the present study and structural data and imaginary frequencies of the transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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