The Mechanism of Hydrocarbon Oxygenate Reforming: C–C Bond Scission, Carbon Formation, and Noble-Metal-Free Oxide Catalysts

Yaroslava Lykhach, Armin Neitzel, Klára Ševčíková, Viktor Johánek, Nataliya Tsud, Tomáš Skála, Kevin C. Prince, Vladimír Matolín, and Jörg Libuda

Abstract: Towards a molecular understanding of the mechanism behind catalytic reforming of bioderived hydrocarbon oxygenates, we explore the C–C bond scission of C2 model compounds (acetic acid, ethanol, ethylene glycol) on ceria model catalysts of different complexity, with and without platinum. Synchrotron photoelectron spectroscopy reveals that the reaction pathway depends very specifically on both the reactant molecule and the catalyst surface. Whereas C–C bond scission on Pt sites and on oxygen vacancies involves intermediately surface carbon species, the reaction occurs without any carbon formation and deposition for ethylene glycol on CeO2(111).

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CeO$_2$(111), via (2) partially reduced CeO$_2$/C$_x$(111) and (3) Pt(111), to the complete model catalyst consisting of (4) Pt nanoparticles supported on CeO$_2$(111). On these four different surfaces we study three different model C$_2$ oxygenates: (A) ethanol (CH$_3$CH$_2$OH), (B) ethylene glycol (HOCH$_2$CH$_2$OH), and (C) acetic acid (CH$_3$COOH). Note that the choice of the catalyst material is motivated by the promising properties reported for Pt/ceria catalysts in bioreforming, and the choice of the model compounds is rationalized by the abundance of hydroxyl and carboxyl functionalities in bio-oils.

On all twelve systems of the resulting catalytic matrix we have performed experiments under identical conditions to explore the reaction mechanisms in molecular detail. This direct comparison of different C$_2$ model oxygenates: (A) ethanol (CH$_3$CH$_2$OH), (B) ethylene glycol (HOCH$_2$CH$_2$OH), and (C) acetic acid (CH$_3$COOH). Note that the choice of the catalyst material is motivated by the promising properties reported for Pt/ceria catalysts in bioreforming, and the choice of the model compounds is rationalized by the abundance of hydroxyl and carboxyl functionalities in bio-oils.

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For ethanol (see Figure 1A1–A4), deprotonation and facile formation of ethoxy groups occurs at low temperature, on both stoichiometric CeO$_2$ and reduced CeO$_2$/C$_x$(111). In part co-adsorbed molecular ethanol deprotonates to ethoxy during annealing to 200 K. The ethoxy decomposes between 500 and 550 K with formation of ethylene and acetaldehyde, as previously shown by Mullins et al. RPES reveals only small changes in the ceria oxidation state (see Figure 2) and only very small contributions from C$_1$ intermediates (methoxy and formate) stemming from side reactions. This illustrates that bioreforming processes that utilize noble-metal-free catalytic materials.

The general surface chemistry observed for the three reactants on the four surfaces is summarized in Figure 1. By using synchrotron-radiation photoelectron spectroscopy (SRPES), the surface species and their interconversion is monitored during adsorption and subsequent thermal treatment. In parallel, we follow the changes of the surface oxidation state of ceria using resonant photoelectron spectroscopy (RPES). Briefly, RPES employs the resonant enhancement ratio (RER) that is a direct measure of the surface oxidation state. For details on sample preparation and experimental methods, see the Supporting Information. Here, we focus on the principal species and mechanism only. Additional data for ethanol, ethylene glycol, and acetic acid are summarized in Figure 2 and will be discussed in detail in forthcoming publications.

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the form of a supported catalyst, that is, Pt/CeO₂ (Figure 1 A4), the catalytic cycle, Pt and ceria sites need to be combined in carbon cannot be removed from Pt thermally. In order to close (Figure 1 A3), primarily via ethoxy to molecularly adsorbed this purpose. In fact, ethanol is efficiently converted on Pt(111) so that an additional noble-metal component is required for (Figure 1 A3), CeO₂ for C–C bond scission is low. This is in sharp contrast to the surface chemistry on reduced CeO₂–x (Figure 1 C2). Here, a strong activity for C–C bond scission is revealed by the appearance of a number of Cₓ surface intermediates, including for example, methoxy and formate, over a broad temperature region (250–550 K). However, there is a price to pay for this high activity, which is the generation of a large amount of surface carbon. These carbon deposits are very stable and cannot be removed by annealing, at least under the conditions of our experiments (Figure 1 C2). Surface carbon is also produced upon reaction of acetic acid on Pt(111) (Figure 1 C3). Here, the reaction pathway involves the formation of acetate that decomposes mostly to ethylenediyn. This finally yields thermally-stable atomic carbon as previously discussed for the case of ethanol. Besides, C–C bond scission in acetate on Pt(111) results in a small fraction of co-adsorbed CO. On the complete model catalyst Pt/CeO₂ (Figure 1 C4) both decomposition pathways are combined and, consequently, the spectra become rather complex. Nevertheless, all intermediates mentioned above can be identified using the simpler surfaces as references. Again, the unique feature of the complete Pt/CeO₂ catalyst is its self-cleaning capability as the result of oxygen reverse spillover and carbon oxidation on Pt sites. However, this process requires relatively high temperatures and even at 700 K, a small fraction of the stable atomic carbon species on ceria remain on the surface (Figure 1 C4).

The most surprising surface chemistry is observed for ethylene glycol (Figure 1 B1–B4). Both on stoichiometric CeO₂ and on reduced CeO₂–x, ethylene glycol deprotonates partially at low temperature. Upon annealing, partial desorption is accompanied by further deprotonation of the remaining molecules to doubly linked ethylenedioxy species (–OCH₂CH₂O–), as previously shown by Chen and Mullins. The ethylenedioxy thermally decomposes at temperatures between 400 and 650 K, without any detectable amount of surface carbon left behind. One may argue that this lack of carbon poisoning may be due to the formation of Cₓ products, similarly as discussed above for ethanol. This is, however, not the case. Chen and Mullins previously suggested that ethylenedioxy can decompose via C–C bond scission and a formate intermediate to CO and CO₂. Our RPES experiments (see Figure 2) reveal the dramatic

![Figure 2. SRPES (top panel) and RPES (middle and bottom panel) revealing the surface chemistry and related surface redox processes during reaction of ethanol, ethylene glycol, and acetic acid on stoichiometric CeO₂(111). The lower panel shows selected valence band spectra, from which the RER was calculated.](image-url)
consequences of this very specific decomposition pathway. Starting from perfectly stoichiometric CeO$_2$ (RER−0), adsorption and reaction of ethanol and acetic acid, that is, those reactants that yield mainly C$_2$ products on CeO$_2$, give rise to very small changes of the surface oxidation state. In sharp contrast, a very strong reduction is observed for ethylene glycol, that is, the reactant for which C–C bond scission occurs. In other words, the surface reaction products, surface hydroxyl and surface formates, efficiently reduce the ceria by removal of lattice oxygen upon decomposition. In fact, strong surface reduction upon conversion of C$_1$ oxygenates has been observed previously for the case of methanol.$^{[19]}$ To close the catalytic cycle, the reduced surface has to be reoxidized, which under realistic conditions can occur by reaction with CO$_2$ or H$_2$O.$^{[10, 20]}$ Note that sustained reaction with ethylene glycol would not be possible, if on partially reduced CeO$_{2-x}$, large amounts of stable carbon would be formed (as observed for acetic acid). This is, however, not the case (Figure 1B2). In accordance with the work of Chen and Mullins, we observe formation of surface enolates (−CH$_2$−CHO−) at temperatures around 500 K, which decompose to C$_2$ products without any surface carbon left behind.$^{[18]}$

What is the influence of adding the noble metal component to the catalyst? The answer is provided in Figure 1B3. Upon heating, ethylene glycol on Pt(111) undergoes partial decomposition to CO via C–C bond scission.$^{[21]}$ The primary intermediates formed in the temperature region between 200 and 350 K include ethylidyne (CCH$_3$), CO, H, and OH. Whereas the latter species desorb upon further heating, ethylidyne shows its typical surface chemistry and leads to formation of atomic carbon. On the complete Pt/CeO$_2$ catalyst both decomposition pathways are combined (Figure 1B4). C–C bond scission now efficiently occurs on both the oxide and the noble metal part of the surface. Carbon is produced as an intermediate of the reaction, however, this surface carbon now stems exclusively from reaction on the Pt nanoparticles and not from the oxide surface. The carbon on the Pt particles is finally removed via oxidative self-cleaning driven by oxygen reverse-spillover from ceria. However depending on the relative rate of carbon formation, ceria reoxidation, and oxygen supply, this mechanism involves the risk of surface carbon accumulation under realistic conditions. Most importantly, the above results show that the conversion of ethylene glycol would also run in the complete absence of Pt without any surface carbon intermediate and, consequently, without the risk of carbon accumulation.

In conclusion, we have performed a systematic model study of the elementary reaction mechanisms of reforming of hydrocarbon oxygenates from bio-derived sources. Simultaneously, we address the materials gap by increasing the chemical and structural complexity of the surface and the chemical complexity gap by introducing different model oxygenates. For each of the twelve reaction systems of the resulting catalytic matrix, we have studied the reaction mechanism and identified the principle surface intermediates, including the redox processes on ceria and the formation of carbon. We find that the reaction pathways depend very specifically on both the model compound and the catalyst surface. This leads to drastic differences with respect to C–C bond activation and carbon poisoning. A summary of the observed mechanisms is schematically shown in Figure 3.

For example, C–C bond scission in ethanol requires Pt and involves intermittent carbon formation and subsequent oxidative self-cleaning. In sharp contrast, C–C bond scission is possible on reduced ceria for acetic acid in the absence of Pt, however, the reaction leads to the formation of very stable carbon deposits. Stoichiometric CeO$_2$(111), on the other hand, is highly active for C–C bond scission in the case of ethylene glycol, leading to strong surface reduction. Importantly, ethylene glycol conversion does not lead to carbon formation, neither on the stoichiometric nor on the reduced surface. In contrast to the oxide channel, the Pt channel involves intermittent carbon formation and, therefore, may potentially lead to catalyst deactivation. These results imply that knowledge-based design of noble-metal free, low-temperature bio-reforming processes may be possible by combination of tailor-made catalysts with tailor-made reactant feeds.

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