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Low-Temperature Conversion of Methane to Methanol on CeO_x/Cu_2O Catalysts: Water Controlled Activation of the C−H Bond

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Supporting Information

ABSTRACT: An inverse CeO_2/Cu_2O/Cu(111) catalyst is able to activate methane at room temperature producing C, CH_x fragments and CO_x species on the oxide surface. The addition of water to the system leads to a drastic change in the selectivity of methane activation yielding only adsorbed CH_x fragments. At a temperature of 450 K, in the presence of water, a $CH_4 \rightarrow CH_3OH$ catalytic transformation occurs with a high selectivity. OH groups formed by the dissociation of water saturate the catalyst surface, removing sites that could decompose CH_x fragments, and generating centers on which methane can directly interact to yield methanol.

Methane is the main component of natural gas. The high abundance of methane in our planet makes it an attractive fuel and building block for the production of fine commodity chemicals.[1] Development of a method for a direct conversion of methane to methanol can lead to a major commercial breakthrough in the use of methane.[1] The partial oxidation of methane to methanol is challenging because the reaction typically progresses all the way to yield CO and/or CO_2.[2]

$$CH_4 + 0.5O_2 \rightarrow CH_3OH \quad (1)$$

$$CH_4 + 0.5O_2 \rightarrow CO + 3H_2 \quad (2)$$

Reactions 1 and 2 are both exothermic, and at temperatures above 600 K reaction 2 becomes the preferred pathway from a thermodynamic viewpoint.[2] Thus, to trap the methanol as a product or intermediate, it is essential to find materials that can activate methane in an efficient way at low temperatures (<500 K).[2,3] This is difficult because the C−H bond in CH_4 has the highest bond energy (104 kcal/mol) among organic compounds. The growing need for inexpensive methods to convert methane to methanol has sparked considerable interest in different approaches that catalyze this process.[3−9] The enzyme methane monooxygenase produces methanol from methane, but cannot be used for industrial-scale reactions.[4,7] In the enzyme, the conversion process is probably carried out by a group of three copper ions.[4] It has been found that copper-exchange zeolites can mimic the nuclearity and reactivity of active sites of the methane monooxygenase.[3,9] In the structure of the zeolites, methanol can be produced by sequential dosing of O_2 and methane, and then flushed out with water.[3] A direct catalytic transformation of methane to methanol is also possible.[9] In this study, we show that a CeO_2/Cu_2O/Cu(111) inverse system is able to activate methane at room temperature and then, with the help of water, performs a catalytic cycle, which is highly selective to the production of methanol.

The system under investigation in this study consists of a film of Cu_2O partially covered with ceria nanoparticles.[10−13] Its morphology has been studied in detail with scanning tunneling microscopy (STM) and low-energy electron microscopy (LEEM).[10,12,13] On the Cu_2O substrate, ceria grows forming small islands (2−5 nm in size) that appear on the terraces of the surface, and large islands (30−50 nm in size) which are embedded in the substrate step edges.[10,13] The large ceria islands have a morphology different from that for the two most stable surfaces of bulk ceria: CeO_2(111) and CeO_2(110).[10,13] At small and medium coverages of ceria (<0.5 ML), the islands are essentially a single layer of ceria {O−Ce−O−Cu staking}.[10,13] At larger coverages, the appearance of islands with two or three ceria layers is observed.[10,13] The oxygen content of the ceria islands easily changes after exposing them to reducing agents or after reoxidation with O_2 or water.[10,13] From previous studies, it is known that the CeO_2/Cu_2O/Cu(111) system is quite active for the dissociation of O_2 and H_2O and is an excellent catalyst for the oxidation of CO (O_2 + $2CO \rightarrow 2CO_2$) and the PROX process.[10,14]

We investigated the dissociation of methane on a series of CeO_2/Cu_2O/Cu(111) surfaces at room temperature. Figure 1 shows C 1s XPS spectra collected after exposing a plain Cu_2O film and a film covered ∼40% with ceria to 1 Torr of CH_4 at 300 K for 5 min. On the plain Cu_2O film, the adsorption of methane is negligible. In contrast, the CeO_2/Cu_2O surface activates methane. Clear peaks are shown in Figure 1 for carbon, CH_x and CO_x species.[15,16] A fraction of the adsorbed methane undergoes complete decomposition: $CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C$. Some of the generated C adatoms react with O atoms from the surface to form CO_x species. Less than a monolayer of methane react with the CeO_2/Cu_2O/Cu(111) surface and the changes in the oxidation state of Cu and Ce were negligible. The ability of CeO_2/Cu_2O/Cu(111) to dissociate water,[13] $H_2O \rightarrow OH + H$, can be used to control

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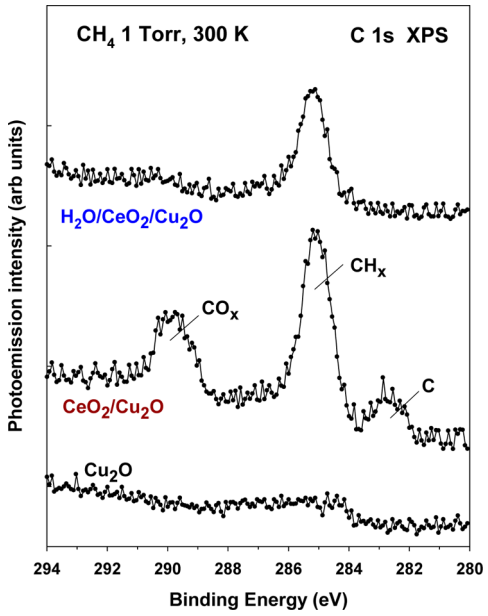

Figure 1. C 1s XPS spectra collected after exposing $Cu_2O/Cu(111)$, $CeO_2/Cu_2O/Cu(111)$ and $H_2O/CeO_2/Cu_2O/Cu(111)$ to 1 Torr of methane at 300 K for 5 min. In the $CeO_2/Cu_2O/Cu(111)$ system, ~40% of the Cu_2O film was covered by ceria. To generate the $H_2O/CeO_2/Cu_2O/Cu(111)$ sample, the $CeO_2/Cu_2O/Cu(111)$ surface was exposed to 50 Langmuir of water at 300 K.

the activation of methane. If water is predosed to CeO_2/Cu_2O, the selectivity toward the production of CH_x increases to 100% (top spectrum in Figure 1). Surface sites that are highly active for the full decomposition of methane are probably blocked by OH groups and the signals for C and CO_x species disappear from the C 1s region. As shown below, this phenomenon can greatly facilitate the conversion of methane into methanol.

The deposited CH_x species in the surfaces of Figure 1 desorbed when the sample temperature was increased from 300 to 400 K. These species are not observed when the $CeO_2/Cu_2O/Cu(111)$ is exposed to methane at 450 K (see Figure S1 in Supporting Information). At this temperature, if water is not present in the background, a large amount of carbon is deposited on the surface (Figure S1) and there is a substantial reduction of the CeO_2 and Cu_2O present in the sample. At 450 K, the mixed-metal oxide is extremely efficient for the cleavage of all the C−H bonds of methane and the generated C and H adatoms react with O sites from Cu_2O and CeO_2 to produce CO and H_2O. When the C-rich surface obtained by exposing CeO_2/Cu_2O to methane at 450 K was treated with water, there was a very large reduction in the intensity of the C features in the C 1s region (Figure S2).

We found that the CH_x and OH groups coadsorbed on $CeO_2/Cu_2O/Cu(111)$ did not react to yield methanol at room temperature. The system cannot overcome the activation barriers associated with the cleavage of HO−surface and H_xC−surface bonds. No reaction was also observed after dosing CH_4 to $OH/CeO_2/Cu_2O$ or H_2O to $CH_x/CeO_2/Cu_2O$ at 300 K. However, at 450 K, we detected formation of methanol. Figure 2 shows data for the conversion of methane into methanol at 450 K under a water-rich environment. Plain Cu_2O is inert as a catalyst. As ceria is added to the copper oxide, there is an increase in the catalytic production of methanol and CO/CO_2 are only secondary products. At the maximum of catalytic activity the ratio of methanol to CO/CO_2 is close to 3:1. The

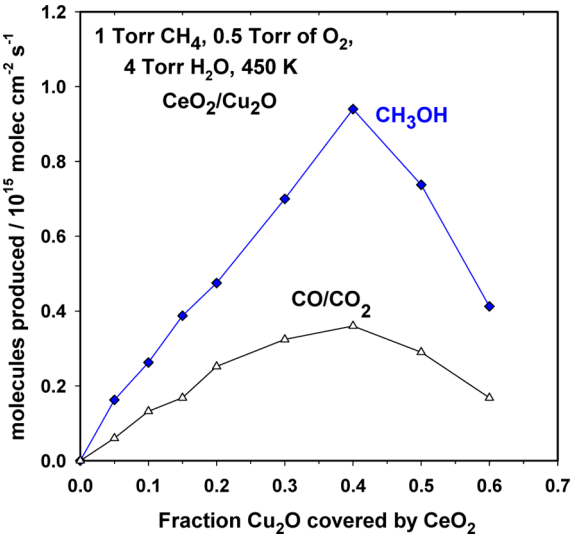

Figure 2. Production of methanol and CO/CO_2 as a function of ceria coverage in a series of $CeO_2/Cu_2O/Cu(111)$ catalysts. The samples were exposed to 1 Torr of CH_4, 0.5 Torr of O_2 and 4 Torr of H_2O at 450 K in a batch reactor.

drop in catalytic activity shown in Figure 2 for large ceria coverages matches well with changes in STM for the growth mode of ceria on $Cu_2O/Cu(111)$.[10,13] When less than 50% of the copper oxide is covered, the ceria islands have only a single layer (i.e., O−Ce−O−Cu staking), but two- and three-layer islands are observed at higher ceria coverages.[10,13] Thus, active sites are probably present at the interface of single-layer ceria islands and Cu_2O.

The pressure of water had a strong effect on the selectivity toward the production of methanol. In Figure 3, we compare

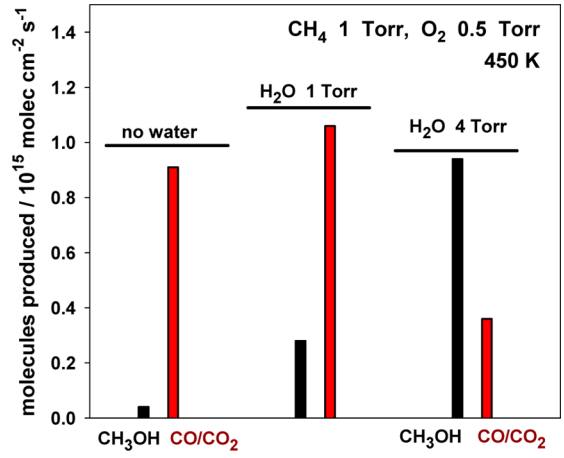

Figure 3. Production of methanol and CO/CO_2 as a function of water pressure on a $CeO_2/Cu_2O/Cu(111)$ catalyst in which ~40% of the Cu_2O was covered by ceria. The samples were exposed to 1 Torr of CH_4, 0.5 Torr of O_2 and 0, 1, or 4 Torr of H_2O at 450 K in a batch reactor.

the amounts of methanol and CO/CO_2 formed as a function of the water pressure in the reactant mixture. If water is not present, the amount of methanol formed is minimal. The highly active sites of the surface are not blocked and the reaction $CH_4 + nO_2 \rightarrow CO/CO_2$ takes place instead of methanol formation. In fact, both reactions are feasible from a thermodynamic viewpoint,[2] but most of the methanol formed may be

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decomposed into CO/CO_2.[3] As water is added, the selectivity toward methanol clearly improves in Figure 3. In a set of experiments, we found that predosing with water blocks the surface sites which are active in $CeO_2/Cu_2O/Cu(111)$ for the dissociation of the methanol molecule. These sites are probably the same sites that carry out the full decomposition of methane in clean $CeO_2/Cu_2O/Cu(111)$. In principle, water could be helping the $CH_4 \rightarrow CH_3OH$ conversion in two ways: Blocking active sites for the dissociation of methanol or by opening a new reaction path for the direct reaction of CH_4 or CH_3 with OH groups. These two possibilities were explored using calculations based on density-functional theory (DFT) (see SI for details).

Postreaction characterization of the catalysts used for the experiments in Figure 3 with XPS showed that their surfaces contained Ce^{4+} and Cu^{1+} (i.e, no reduction of the components in the $CeO_2/Cu_2O/Cu(111)$ starting catalysts). The interaction of methane with $Cu_2O/Cu(111)$ and $CeO_2/Cu_2O/Cu(111)$ surfaces was investigated employing models developed in previous studies.[10,17] Top and side views of these models are shown in Figure S3. From the results in Figure 2 and previous STM studies,[10,13] we know that the active phase of the catalyst contains single-layer ceria islands dispersed on Cu_2O. The calculated adsorption energies of reaction intermediates on $Cu_2O/Cu(111)$ and $CeO_2/Cu_2O/Cu(111)$ are listed in Table S1. One can see that the deposition of CeO_2 leads to a stabilization of the CH_3 and OH intermediates. The calculations indicate that on both surfaces, methane is only physisorbed. The dissociation of methane on a $Cu_2O/Cu(111)$ surface is problematic (reaction energy of 0.30 eV and activation barrier of 1.60 eV) in agreement with the XPS data in Figure 1. With the presence of CeO_2 nanoparticles on the Cu_2O film, the interfacial Ce^{4+} sites help methane dissociation to methyl (reaction energy of −1.23 eV and activation energy of 0.51 eV) at the interfacial O sites (Figure 4). Thus, methane

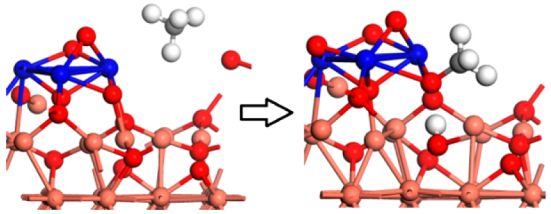

Figure 4. Calculated adsorption geometry for methane adsorption and dissociation on $CeO_2/Cu_2O/Cu(111)$. The blue, brown, red, gray and white balls represent Ce, Cu, O, C and H atoms, respectively.

can dissociate on $CeO_2/Cu_2O/Cu(111)$ at room temperature. The calculated activation energy is much smaller than typical values found on metals,[8,18] A key factor is the participation of the O centers of $CeO_2/Cu_2O/Cu(111)$ in C−H bond breaking (Figure 4). The calculated activation energy of 0.51 eV compares well with activation energies found for systems that can activate methane at room temperature like Zn modified H-ZSM-5[6] and Ni dispersed on ceria.[15]

The deposition of CeO_2 also helps water dissociation. On $Cu_2O/Cu(111)$, water dissociation is an activated process (reaction energy of 0.33 eV and activation energy of 0.84 eV). The presence of CeO_2 enables a spontaneous O−H bond cleavage. Although the dissociation of methane on CeO_2/Cu_2O is energetically favorable; yet it cannot compete with water dissociation at the same sites. Therefore, surface hydroxylation is expected, and water should have strong effect in the selectivity of the reaction processes. The calculations indicate that following the Langmuir−Hinshelwood (LH) mechanism the reaction involving dissociated CH_3(ads) at the interfacial O sites and OH(ads) at Ce sites to yield methanol is rather difficult (reaction energy of 0.48 eV and activation barrier of 2.80 eV, Figure S4). This is likely hindered by the high stability of CH_3(ads) at the oxygen sites. The reaction could follow less direct paths in which methyl reacts with O to form CH_3O and then is hydrogenated to form methanol, as proposed in other theoretical studies.[6,9] One interesting route found in the DFT calculations involves a direct dissociation of methane on the dissociated OH groups bound to Cu_2O or CeO_2/Cu_2O via the Eley−Rideal (ER) mechanism, see Figures 5 and S5 plus Table

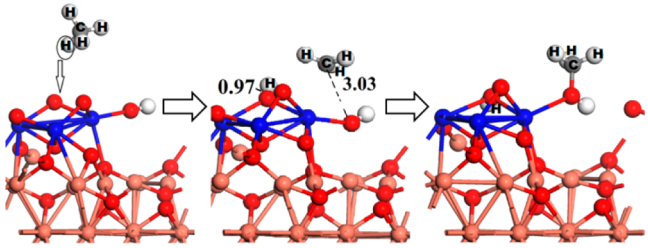

Figure 5. Structures of initial (left), transition (middle) and final (right) states for methanol synthesis involving dissociative adsorption of methane over the OH(ads) species on $CeO_2/Cu_2O/Cu(111)$. The blue, brown, red, gray and white balls represent Ce, Cu, O, C and H atoms, respectively.

S2. Following this pathway on $HO/CeO_2/Cu_2O/Cu(111)$, the dissociation of methane leads to the direct formation of methanol at the OH anchored at Ce sites and avoids the cleavage of strong O−CH_3 bonds. As a result, the methanol formation is greatly facilitated (reaction energy of −0.75 eV and activation energy of 1.22 eV, Figure S5). The calculations show that without the use of the OH bound to Ce sites, the methyl species from methane dissociation at interfacial Ce sites are too stable to be oxidized, rather preferring further decomposition to carbon. However, this is not the case for $Cu_2O/Cu(111)$. Although the surface hydroxylation is also likely to occur, the direct methane dissociation on OH(ads) is highly activated with the barriers of at least 1.93 eV depending on the position of OH(ads) (Figures S6 and S7). On $Cu_2O/Cu(111)$, the OH is embedded on a hexagonal cavity of the oxide surface (Figure S6); a configuration that makes difficult interactions with methane (Figure S7). This is not a problem in the case of OH bound to $CeO_2/Cu_2O/Cu(111)$, Figure 5. The high activity of the OH(ads) species bound to $CeO_2/Cu_2O/Cu(111)$ is also associated with a hybridization between O 2p orbitals and 4f orbitals of Ce^{4+}. It results in an OH species with intense high-lying O 2p states, which are more active for attracting and dissociating methane than OH(ads) bound to $Cu_2O/Cu(111)$, see Figure 6.

In summary, we have found that a CeO_2/Cu_2O interface is able to bind and dissociate methane at room temperature. In this aspect, it mimics the activity of the methane monooxygenase[4] and a few inorganic systems.[5,6,19] The products of the adsorption process on CeO_2/Cu_2O are C, CH_x fragments and CO_x species. The addition of water to the system leads to a drastic change in the selectivity of methane activation yielding only adsorbed CH_x fragments. At a temperature of 450 K, in the presence of water, a $CH_4 \rightarrow CH_3OH$ catalytic trans-

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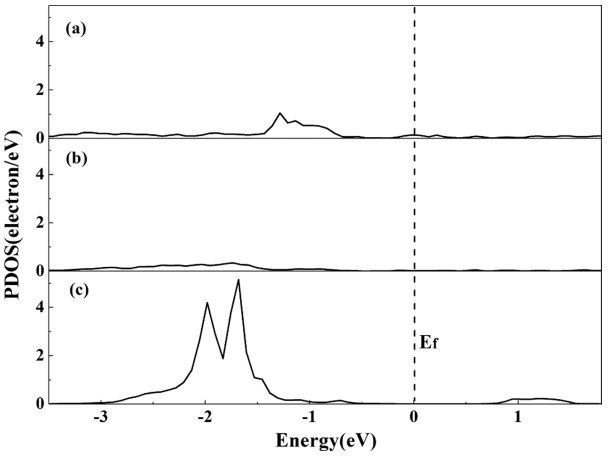

Figure 6. O 2p PDOS for OH(ads) in the ring center (a) and at atop (b) sites of Cu ions on $Cu_2O/Cu(111)$, and top of Ce ions on $CeO_2/Cu_2O/Cu(111)$ (c). States with high intensity are observed only in the case of $OH/CeO_2/Cu_2O/Cu(111)$.

formation occurs with a high selectivity. OH groups formed by the dissociation of water saturate the catalyst surface, removing sites that could decompose CH_x fragments, and generating centers, which have special electronic properties, on which methane can directly interact to yield methanol.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08668.

Experimental procedures; C 1s XPS spectra collected after dosing methane and water to a CeO_2/Cu_2O system at 450 K; details for the DFT calculations; structures of the models used in DFT calculations to describe bare $Cu_2O/Cu(111)$ and $CeO_2/Cu_2O/Cu(111)$ surfaces systems as well as some of the reaction intermediates and transition states involved (PDF)

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Notes

The authors declare no competing financial interest.

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