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Article

Role of surface frustrated Lewis pairs on reduced $\text{CeO}_2(110)$ in direct conversion of syngas

Zheng-Qing Huang, Teng-Hao Li, Bolun Yang, Chun-Ran Chang *

Shaanxi Key Laboratory of Energy Chemical Process Intensification, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China

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ABSTRACT

Direct syngas conversion to light olefins on bifunctional oxide-zeolite (OX-ZEO) catalysts is of great interest to both academia and industry, but the role of oxygen vacancy (V_O) in metal oxides and whether the key intermediate in the reaction mechanism is ketene or methanol are still not well-understood. To address these two issues, we carry out a theoretical study of the syngas conversion on the typical reducible metal oxide, CeO_2 , using density functional theory calculations. Our results demonstrate that by forming frustrated Lewis pairs (FLPs), the V_O s in CeO_2 play a key role in the activation of H_2 and CO. The activation of H_2 on FLPs undergoes a heterolytic dissociative pathway with a tiny barrier of 0.01 eV, while CO is activated on FLPs by combining with the basic site (O atom) of FLPs to form CO_2^{2-} . Four pathways for the conversion of syngas were explored on FLPs, two of which are prone to form ketene and the other two are inclined to produce methanol suggesting a compromise to resolve the debate about the key intermediates (ketene or methanol) in the experiments. Rate constant calculations showed that the route initiating with the coupling of two CO^* into OCCO^* and ending with the formation of ketene is the dominant pathway, with the neighboring FLPs playing an important role in this pathway. Overall, our study reveals the function of the surface FLPs in the activation of H_2 and CO and the reaction mechanism for the production of ketene and methanol for the first time, providing novel insights into syngas conversion over OX-ZEO catalysts.

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1. Introduction

Production of light olefins (C_2 – C_4 olefins) via non-oil-based processes has motivated an increasing number of studies due to the growing demand for these key molecular building blocks and the concern regarding the diminishing oil reserves [1]. A promising route that first generates syngas (H_2 and CO) from alternative resources such as natural gas, coal, and renewable

biomass and then converts the syngas to light olefins in direct or indirect processes has been widely investigated [1,2]. Several indirect processes for converting syngas to light olefins have been developed and even commercialized, such as the methanol to olefins (MTO) process, but still have drawbacks of high equipment cost and high energy consumption due to the use of multiple steps in the process [1,3,4]. Recently, the direct Fischer-Tropsch to olefins (FTO) process using Fe- or Co-based cat-

* Corresponding author. E-mail: changcr@mail.xjtu.edu.cn

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alysts has attracted significant interest [5–8]. However, due to the Anderson-Schulz-Flory (ASF) limit in Fischer-Tropsch synthesis, the maximum selectivity of C₂–C₄ olefins cannot exceed 60% [7,8].

The limited selectivity for the process based on the Fe- or Co-based catalysts is mainly attributed to the uncontrollable coupling of the CH_x species at the same active sites where CO activation occurs, necessitating the development of novel strategies for the separation of CO activation and C–C coupling on different active sites. Bao *et al.* [9] reported an OX-ZEO (oxide-zeolite) process that separates CO activation on a reduced mixed metal oxide (ZnCrO_x) and C–C coupling in the zeolite (MSAPO) pores to reach a high C₂–C₄ olefins selectivity of 80% at a CO conversion rate of 17% at 673 K. Meanwhile, Wang *et al.* [10] developed a bifunctional catalyst composed of Zr–Zn oxide and SAPO-34 molecular sieve that offers a high C₂–C₄ olefins selectivity of 74% at a CO conversion rate of 11% at 673 K. Since these two pioneering works, intense studies of direct syngas conversion using the bifunctional OX-ZEO catalysts have been carried out. To date, various bifunctional catalysts have been developed by modifying both metal oxides and zeolites in order to improve the catalytic performance [11–17]. The increasing high selectivity is enabling the OX-ZEO process to become a potential competitor for industrial processes such as FTO and MTO [18]. In addition, further research effort has focused on the selective production of other hydrocarbons such as aromatics [19–25], and on the other hand, an increasing number of studies have been performed on the direct hydrogenation of CO₂ to light olefins using similar OX-ZEO catalysts [26–29].

Despite the significant progress achieved for the direct syngas conversion to light olefins over the OX-ZEO catalysts, some critical issues remain unresolved. For OX-ZEO catalysts, the mole ratio of the two metal elements in the mixed oxide, the role of the oxygen defects in the oxide, the density of the Brønsted acid sites of the zeolites, and the proximity of the oxide and zeolite are the main factors controlling the CO conversion and light olefin selectivity that are still under study [13,17]. Here, our research focuses on metal oxides since H₂ and CO are first converted to intermediates on the metal oxide surfaces [9,10]. The two main issues related to our study are as follows. (1) The role played by the oxygen vacancies (V_{Os}) in metal oxides has not been fully elucidated even though intense experimental studies including the first two pioneering works mentioned above have indicated the importance of V_{Os} [9,10]. While studies performed to date have demonstrated that oxygen vacancies are mainly responsible for CO activation [11,13], detailed studies at the molecular level are needed to obtain deeper understanding of the role played by V_{Os}. (2) The debate about the reaction mechanism of CO hydrogenation for the formation of key intermediates such as ketene or methanol remains unresolved. Despite the partial evidence obtained by experimental studies, the two possible mechanisms proceeding via either the ketene or methanol intermediates are not fully understood [9,10]. Hence, a mechanistic understanding of the generation of different intermediates at an atomic level is highly desirable.

To address the above-described issues, the selection of a suitable metal oxide as the research model is critical. Based on the experiments, the mixed metal oxides should be the first choice, but their crystal structures are too complex for use as a theoretical model [30]. Moreover, searching more complicated surface structures is still challenging due to the high computational cost. Interestingly, recent studies reported that the unary oxides such as MnO and ZnO [11,16] also perform as well as the binary oxides such as ZnCrO_x, indicating that a unary oxide is sufficiently active for use in the OX-ZEO catalyzed direct syngas conversion to light olefins. Therefore, reducible unary oxides are considered in our studies because this approach avoids the need to treat the complex surface structures of mixed metal oxides.

Since the pioneering work by Stephan *et al.* [31,32] in 2006 on the reversible metal-free hydrogen activation, the novel concept of frustrated Lewis pairs (FLPs) where the Lewis acid and Lewis base are sterically encumbered has attracted significant research interest [31] and homogenous FLPs have been demonstrated to activate syngas and generate formyl and alkoxy intermediates [32]. However, the utilization of the homogeneous molecular-based FLPs is hindered by the problematic and costly catalyst recycling. In recent years, the solid/surface frustrated Lewis pairs constructed based on the V_{Os} of reduced metal oxides have been shown to be able to circumvent the drawbacks of homogeneous FLPs, and have been reported in hydrogen dissociation, CO₂ hydrogenation, and methane dissociation [33–39]. Therefore, we expect that such kind of FLPs based on V_{Os} can also play an important role in the oxide-catalyzed syngas conversion. The present study focuses on the role of surface FLPs/oxides in the activation and conversion of syngas to intermediates (ketene or methanol) which in turn can reveal the role of V_{Os} in the OX-ZEO catalysis of syngas conversion as mentioned above. The surface FLPs are constructed on ceria due to the easy release/storage of oxygen by forming/filling oxygen vacancies [40]. As shown in Fig. 1(right), by removing two O atoms on CeO₂(110), the two adjacent surface Ce cations next to V_O acting as the Lewis acid and one neighboring O anion acting as the Lewis base construct the FLP sites. The distance between the acid site (coordinatively unsaturated Ce) and the base site (surface O) is ~4 Å, longer than that of the Ce–O bond (~2 Å) in the classical Lewis pairs (CLPs) on stoichiometric CeO₂(110) shown in Fig. 1(left). In addition, the two FLP sites in Fig. 1 are located close to each other. The structures of FLPs on reduced CeO₂(110) have been elucidated by both static density functional theory (DFT) calculations and ab initio molecular dynamics simulations under reaction conditions [37,39]. Experimentally, it was shown that the addition of a trace amount of either Lewis base pyridine or Lewis acid pyrrole can completely quench the hydrogenation reactivity due to the blockage of the surface Lewis acidic or basic sites by these small molecules, respectively, indirectly suggesting the existence of FLPs [39]. More details about the FLPs on ceria surfaces are available in the previous reports [37–39]. Moreover, previous studies have reported that pure ceria was among the most promising catalysts for isosynthesis in which syngas is converted to hydrocarbons [41,42]. In a recent study of syngas

Fig. 1. Schematic of CLPs on stoichiometric $\text{CeO}_2(110)$ and FLPs on reduced $\text{CeO}_2(110)$. Yellow and red spheres represent Ce and O atoms, respectively. The Lewis acidic sites (Ce atom) and basic sites (O atom) in CLPs and FLPs are labeled by magenta and blue circles, respectively. The label “ V_O ” in green circles denotes the position of the oxygen vacancy.

conversion, the pure ceria with HZSM-5 achieved high selectivity to C_{2-4} hydrocarbons and high CO conversion, indicating the possibility of syngas conversion on ceria surfaces [21]. Based on the catalytic features of solid FLPs and syngas conversion on pure ceria, it is desirable to study the direct syngas conversion to key intermediates at the FLP sites on the reduced ceria surface.

In this work, we first studied the activation of the H_2 and CO molecules at the FLP sites on the reduced $\text{CeO}_2(110)$ surface. Then, four pathways for the conversion of H_2 and CO to ketene or methanol at a reaction temperature of 673 K were explored, and the dominant pathway was identified by calculating the Gibbs free energy of activation and the rate constants of the elementary steps.

2. Computational details

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [43–45] with the electron-ion interaction represented by the projector-augmented wave pseudopotentials [46]. The spin-polarized Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was used as the exchange-correlation functional [47], and the plane-wave kinetic energy cutoff was set to 400 eV. The DFT + U method with an effective $U = 4.5$ eV was used to treat the on-site Coulomb and exchange interaction of the strongly localized Ce 4*f* electrons [48–50]. The van der Waals dispersion forces were considered using Grimme’s zero damping DFT-D3 method to account for the weak interactions between the adsorbates and the surfaces [51]. The first Brillouin zone k -point sampling utilized the Monkhorst-Pack scheme with a $7 \times 7 \times 7$ mesh for the bulk and a $1 \times 1 \times 1$ mesh for the $\text{CeO}_2(110)$ surfaces [52]. The energy and force criteria for convergence of the energy and structure optimization were set to 10^{-5} eV and 0.02 eV $\text{\AA}^{-1}$, respectively. The nudged elastic band combined with the minimum-mode following dimer method was used to search the transition state structures of the elementary steps [43,53]. All of the transition states were identified using vibrational analysis. The reaction energy, ΔE , was defined as the energy difference between the product and the corresponding reactant. The activation energy, E_a , was defined as the energy difference between the transition state and

the initial state, and the details regarding the calculation of the Gibbs free energy and rate constant are found in the Supporting Information. The calculations of the Gibbs free energy of reaction, ΔG , and the Gibbs free energy of activation, G_a , were similar to those of the reaction energy and activation energy, respectively. Atomic charges were computed using the atoms-in-molecules scheme proposed by Bader [54]. The crystal orbital Hamilton population (COHP) curves were generated with LOBSTER [55–58]. The relevant details about these methods can be found in our previous report [37].

The calculated lattice parameter for bulk CeO_2 was 5.43 $\text{\AA}$ which is very close to the experimental value of 5.41 $\text{\AA}$ [59]. Since our previous studies concluded that the construction of FLPs by only regulating the surface V_O s on $\text{CeO}_2(111)$ is unsuccessful and the $\text{CeO}_2(110)$ surface is more stable than the $\text{CeO}_2(100)$ surface as indicated by their respective surface energies [37,38], the $\text{CeO}_2(110)$ surface was selected. The surface was modeled using a periodic five-layer slab as shown in Fig. 2(a). Similar to previous work [37], the $p(2 \times 3)$ supercell was adopted to study syngas conversion. The bottom three layers of the slab were fixed at the bulk positions, and the top two layers with adsorbates were allowed to relax. Only the top-surface oxygen vacancies are included in the calculations described below [37]. Our previous study found that reduced $\text{CeO}_2(110)$ with two V_O s in a $p(2 \times 3)$ supercell can form dynamic FLPs via thermal fluctuations and reactant adsorption [37]. Therefore, the calculations related to the FLPs are based on the surface structure shown in Fig. 2(b) with one O atom next to V_O at the original bulk position in the plane (P site) and another O atom next to V_O at the bridge site of the Ce atoms (B site). The optimized structure shown in Fig. 2(b) is the most stable structure with FLP sites. As shown in Fig. S1, our calculated results indicate that compared to the V_O formation through the generation of O_2 and H_2O , the surface oxygen vacancy formation through the generation of CO_2 from CO oxidation is the most thermodynamically favorable process at 673 K. In addition, the calculations related to CLPs are based on the surface structure shown in Fig. 2(a). All of the slab structures corresponding to the data in Figs. 3 and 5–8 are displayed in the Supporting Information with Ce^{3+} ions labeled.

3. Results and discussion

3.1. Activation of H_2 and CO on FLPs

First, the activation of H_2 and CO at the FLP sites on reduced

Fig. 2. (a) Optimized structure of the stoichiometric $\text{CeO}_2(110)$ surface with five atomic layers in the $p(2 \times 3)$ supercell. (b) Optimized structure of the reduced $\text{CeO}_2(110)$ surface with two V_O s in a $p(2 \times 3)$ supercell. Only the top two layers are shown in the top view.

Fig. 3. Adsorption energies (a) and optimized structures (b) of H₂, CO and C₂H₄ on CLPs and FLPs. H(Ce) represents the H atom bound to Ce atoms. H(O) represents the H atom bound to O atom. The structures in black and red frames present the adsorption states on CLPs and FLPs in Fig. 3(a), respectively. The values shown in (b) are the Bader charges of the selected atoms in the parentheses. (c) Potential energy surface and the variations of the H–H bond length along with hydrogen dissociation reaction coordinate on FLPs and CLPs.

CeO₂(110) was explored and compared to that at the CLP sites on stoichiometric CeO₂(110). As shown in Fig. 3(a), the molecular adsorption of H₂ on FLPs is weak (−0.27 eV), but is still stronger than that on CLPs (−0.14 eV). As indicated by the Bader charges of the H₂ molecule presented in Fig. 3(b) and Table S1, a larger electron transfer from the surface to H₂ on FLPs was found. As shown in Fig. 3(c), the length of the H–H bond increased significantly from 0.75 Å in the gas-phase to 0.80 Å on FLPs, in comparison to a slight increase of 0.01 Å on CLPs. Both the atomic charge and bond length suggest that H₂ is more effectively activated on FLPs than on CLPs. Further dissociation of H₂ at the FLP sites is almost barrierless ($E_a = 0.01$ eV) and thermodynamically favorable with reaction energy of −0.53 eV, in good agreement with the previous studies [38,39]. However,

both the activation energy (0.57 eV) and reaction energy (0.41 eV) are much higher on CLPs. Importantly, the adsorption of H₂ on FLPs is dissociative adsorption, producing one hydride (H_a in Fig. 3(b)) and one proton (H_b in Fig. 3(b)). Our previous study has found that the hydride can be stable at the FLP sites and serves as an active intermediate in the hydrogenation reactions, while the hydride at the CLP sites can easily transfer to the nearby O atoms and form strong O–H bond [38]. In addition, the formation of hydride on reduced ceria has also been evidenced experimentally [60,61].

Here, we carried out an analysis of the crystal orbital Hamilton population in order to further study the activation of H₂ on FLPs [55–58]. The negative projected COHP (pCOHP) curves presented in Fig. 4(a) show that the lowest unoccupied H–H orbital (the partial charge density from 2.0 to 3.0 eV in Fig. 4(b)) on FLPs is closer to the Fermi level than that on CLPs, suggesting an increased ability of H₂ on FLPs to accept electrons. More importantly, in the enlarged local pCOHP shown in Fig. 4(a), a slightly negative peak in the range from −3.0 to −1.0 eV corresponding to the occupied antibonding state is observed on FLPs, suggesting the H–H bond is weakened by electron transfer from the surface to the H–H antibonding orbital. The electrons in the energy range from −3.0 to −1.0 eV are mainly located around the hydride (H_a) close to the Ce ions as shown in Fig. 4(b), due to the local electric field of the metal oxide surface. Overall, the above analysis indicates that the electron transfer from the surface to the antibonding molecular orbital of H₂ and the local electric field both contribute to the activity of Lewis pairs.

Previous studies have reported that chemical adsorption of CO₂ on metal oxide surfaces is strong and can form CO₃^{2−} group [62–64]. Similarly, CO on CeO₂(110) can also bind with two surface O atoms to form a CO₃^{2−} group. The strongest adsorption on CLPs releases heat of 3.50 eV as shown in Figs. 3 and S2. The formation of a stable CO₃^{2−} group with a large adsorption energy suggests that it is difficult for the subsequent hydrogenation steps to form methanol or ketene to occur. Fortunately, CO can form a bent CO₂ group when inserting into FLPs as shown in Figs. 3(b) and S3, and as supported by a previous

Fig. 4. (a) Negative pCOHP curves for the H–H bonds on CLPs (black) and FLPs (red). The enlarged local pCOHP curves inserted in the panel correspond to the region labeled by magenta dashed circles. (b) Partial charge density maps for adsorbed H₂ on FLPs calculated using the energy ranges of $2.0 \leq E \leq 3.0$ eV (top) and $-3.0 \leq E \leq -1.0$ eV (bottom). (c) Negative pCOHP curves for C–O bonds on CLPs (black) and FLPs (red). (d) Partial charge density maps for adsorbed CO on FLPs calculated using the energy ranges of $1.6 \leq E \leq 2.8$ eV (top) and $-2.0 \leq E \leq 0.0$ eV (bottom). The Fermi levels of the CeO₂ slabs are set to zero in this figure.

Fourier-transform infrared spectroscopy study of CO adsorption on CeO₂ [65]. The adsorption energy (absolute value) decreases to −1.68 eV, and the atomic charges of the CO₂ group at FLPs is −1.38 e (Fig. 3(b) and Table S2), close to that of the CO₃^{2−} group at CLPs (−1.58 e), while the number of the surface Ce³⁺ ions remains the same after CO adsorption (Fig. S3), suggesting the formation of a CO₂^{2−} group.

The electronic structures of the CO₂^{2−} group on FLPs and the CO₃^{2−} group on CLPs are analyzed (Fig. 4). The pCOHP curves for the three C–O bonds in the CO₃^{2−} group reveal that the bonding orbitals (−pCOHP > 0) are below the Fermi level and the antibonding states (−pCOHP < 0) are almost above the Fermi level, indicative of strong C–O bonds. For the two curves of the CO₂^{2−} group, two sharp peaks close to the Fermi level are observed at −0.8 eV and at 2.3 eV. The occupied antibonding orbitals ranging from −2.0 to 0.0 eV reflect the weaker C–O bonds on FLPs. Therefore, the COHP analysis indicates that two C–O bonds in the CO₂^{2−} group are weakened and the chemically adsorbed CO* on FLPs can be more active in the subsequent reactions.

By calculating the adsorption energies and analyzing the electronic structures of H₂ and CO, we found that by forming surface FLPs, the oxygen vacancy can serve as catalytic centers for the dissociation of hydrogen to hydride and proton and for binding CO to form active CO₂^{2−} groups. Moreover, as shown in Fig. 3(a) the adsorption of ethylene which is a product of syngas conversion is weaker on FLPs (−0.49 eV) than both the dissociative adsorption of H₂ (−0.80 eV) and adsorption of CO (−1.68 eV) on FLPs, indicating that the adsorption of H₂ and CO is advantageous compared to that of C₂H₄ on the reduced CeO₂(110) surface.

3.2. Conversion of syngas to ketene or methanol on FLPs

In the previous section, we only considered the activation of a single molecule at a single FLP site, namely either the transformation of H₂ into H⁺ and H[−] or the transformation of CO into CO₂^{2−}. To reveal the hydrogenation mechanism, four pathways classified by the adsorption states and the interactions between H₂ and CO at the beginning of the reactions were proposed. In pathway I, H₂ and CO first occupy two neighboring FLP sites (see the FLPs in Fig. 1) and then the surface reactions proceed. In pathway II, two CO occupy two neighboring FLP sites and then C–C coupling occurs. In pathway III, the H₂ first dissociates into a proton and hydride and then CO attacks the adsorbed hydride. In pathway IV, the CO first adsorbs at the FLP sites and then the H₂ directly dissociates at the Lewis pairs formed by CO₂^{2−} and surface ions. In the following, these four syngas conversion pathways at the reaction temperature of 673 K will be discussed in detail.

3.2.1. Pathway I for ketene production

As shown in Fig. 5(a), the activations of both CO and H₂ are facile with an exothermic adsorption free energy of −0.61 eV for CO adsorption and a small *G_a* of 0.22 eV for hydrogen dissociation. Then, the active hydride attacks the C atom to form CHO* (from A3 to A4); this step is also facile with a low *G_a* of 0.59 eV

and an exothermic ΔG of −1.65 eV. The second CO occupies the vacant position left by the hydride (state A5) and then binds a proton to form another CHO* (state A6). However, the second hydrogenation (from A5 to A6) needs to overcome a *G_a* of 1.25 eV. After a rotation of CHO*, the two adsorbed CHO* occupy two neighboring FLP sites, respectively, forming the most stable intermediate (state A7) in pathway I. To continue the reaction, H₂ dissociates at the nearby CLP sites (from A8 to A9) with a *G_a* of 0.90 eV. The subsequent hydrogenation of CHO* by a hydride has a *G_a* of 1.15 eV. The surface C–C coupling occurs between CHO* and CHO* (from A10 to A11) with a moderate *G_a* of 0.84 eV and an exothermic ΔG of −0.38 eV. Then, the newly formed OCHCHO* successively undergoes two facile steps, namely breaking of the C–O bond (from A11 to A12) and hydrogen transfer between two C atoms (from A12 to A13), to form CH₂CO* (ketene). To release the ketene into the gas phase, two C–O bonds must be broken which is difficult due to a *G_a* that is as high as 1.68 eV. After ketene desorption, the generation of water into the gas phase (from A15 to A18) proceeds through a three-step pathway with a *G_a* as high as 1.27 eV. For pathway I, the rate-determining step is the cleavage of the C–O bond for the release of CH₂CO* into the gas phase.

3.2.2. Pathway II for ketene production

Pathway II starts from two CO molecules adsorbed at two neighboring FLP sites with an adsorption free energy of −0.45 eV (state B2) as shown in Fig. 6. As the two adsorbed CO* are activated by FLPs, the coupling of two CO* to form OCCO* only needs to overcome a small *G_a* of 0.28 eV (from B2 to B3). Similarly, the coupling of two adsorbed CO molecules has been reported in the studies of the electrocatalytic reduction of CO and CO₂ on Cu(100) using density functional theory investigations [66] and Fourier transform infrared spectroscopy [67]. Since

Fig. 5. (a) Gibbs free energy diagram for the conversion of H₂ and CO to CH₂CO and H₂O on FLPs via pathway I at 673 K. The zero energy reference corresponds to the sum of Gibbs free energies of CO_(g), H_{2(g)}, and the reduced CeO₂(110) surface in Fig. 2(b). (b) Corresponding optimized structures of the intermediates in (a). The structures of the transition states are shown in Fig. S8.

Fig. 6. (a) Gibbs free energy diagram for the conversion of H_2 and CO to CH_2CO and H_2O on FLPs via pathway II at 673 K. (b) Corresponding optimized structures of the intermediates in (a). The structures of the transition states are shown in Fig. S9.

the FLPs are occupied by OCCO^* , the dissociation of H_2 (from B4 to B5) occurs at the nearby CLP sites with a G_a of 1.18 eV. The hydride first binds the nearby C_a atom (from B6 to B7), and then transfers to another C_b atom (from B7 to B8). Since OCHCO^* mainly occupies a single FLP site, the surface OH group can diffuse above the two Ce atoms (from B8 to B9) to form a hydrogen bond with the O atom in OCHCO^* . After the H atom returns back to C_a atom from the C_b atom (from B9 to B10), the proton almost spontaneously transfers from the surface OH group to the O atom in OCHCO^* (from B10 to B11). The addition of the first H_2 to OCCO^* (from B3 to B11) is facile because the highest G_a is only 1.05 eV. For the OCCHOH^* in state B11, the bond length between the C_a atom and the O atom of hydroxyl is 1.48 Å, longer than the C–O bond in methanol (1.43 Å), indicating that the $\text{C}_a\text{--O(H)}$ bond is weak. Hence, we consider the H_2 dissociation between the O atom of hydroxyl and the C_b atom, which is a $\text{C}_b\cdots\text{O}$ FLP with a distance of 2.44 Å. The reaction (from B11 to B12) following the Eley-Rideal mechanism needs to overcome a high G_a of 1.68 eV and leads to the formation of one adsorbed H_2O and addition of one H atom to C_b atom. After the desorption of water (from B12 to B13) and transfer of the H atom (from B13 to B14), the adsorbed CH_2CO^* forms. The subsequent cleavage of two C–O bonds to release the ketene into the gas phase needs to overcome a G_a that is as high as 1.21 eV. Unlike for pathway I, the rate-determining step in pathway II is the simultaneous dissociation of the second hydrogen molecule and the cleavage of one C–O bond to form adsorbed water.

3.2.3. Pathway III for methanol production

In the initial stages of pathways I and II, the H_2 and CO molecules chemically adsorb on FLPs and then the surface reaction occurs. In pathway III, the CO initially physically adsorbs on the top site of Ce atom and then binds with the hydride on FLPs

Fig. 7. (a) Gibbs free energy diagram for the conversion of H_2 and CO to CH_3OH on FLPs via pathway III at 673 K. (b) Corresponding optimized structures of intermediates in (a). The structures of the transition states are shown in Fig. S10.

(from C3 to C4) to form CHO^* . The hydrogenation of CHO^* by a proton (from C4 to C5) generates CH_2O^* and the further rotation stabilizes the CH_2O^* by forming the second C–O bond with the O atom (state C6) of FLPs. The second H_2 dissociates at another FLP site with a low G_a of 0.20 eV. The G_a of the elementary steps from state C0 to state C8 (CH_2O^* and 2H^* at two neighboring FLP sites) are no greater than 0.50 eV. However, the subsequent transfer of the hydride to the O atom of CH_2O^* (from C8 to C9) must overcome a high G_a of 1.70 eV. Then, the

Fig. 8. (a) Gibbs free energy diagram for the conversion of H_2 and CO to CH_3OH on FLPs via pathway IV at 673 K. (b) Corresponding optimized structures of intermediates in (a). The structures of the transition states are shown in Fig. S11.

transfer of the H atom from the O atom to the C atom to form CH_3O^* (from C9 to C10) is favorable both kinetically (0.21 eV) and thermodynamically (−0.40 eV). After two steps of the surface diffusion of OH^* and CH_3O^* , the breaking of the C–O bond and formation of the O–H bond to generate and release CH_3OH into the gas phase need to overcome a ΔG of 1.00 eV. Overall, the rate-determining step is the hydrogenation of the adsorbed CH_2O^* with a G_a of 1.70 eV.

3.2.4. Pathway IV for methanol production

Similar to the direct attack of the dissociated H_2 by CO in the initial stage of pathway III, the dissociation of intact H_2 by the chemically adsorbed CO was studied in pathway IV. The dissociation process is assisted by the Lewis pairs between the O atom in CO and the surface Ce ion, indicated by the transition state structure shown in Fig. S11. The process results in the formation of CHOH^* with a high G_a of 1.97 eV. The dissociation of the second H_2 occurs between the C atom and a Ce cation (from D4 to D5) to form CH_2OH^* that has a low G_a of 0.62 eV. The transfer of the H atom from the O atom to the C atom to form CH_3O^* is also facile with a low G_a of 0.46 eV. The surface transfer of the H atom (from D7 to D8) has a high G_a of 1.61 eV. Similar to pathway III, the generation and release of CH_3OH into the gas phase has a ΔG of 1.20 eV. Overall, the dissociation of the first H_2 with a G_a of 1.97 eV is still the rate-determining step in pathway IV.

3.2.5. Comparison of the four pathways

The four syngas conversion pathways discussed above present two routes for ketene production and two routes for methanol generation as shown in Fig. 9. Comparing the G_a values for the elementary steps shows that pathway IV is distinctly more difficult than the other three routes due to the high G_a of its rate-determining step (1.97 eV). The G_a values of the rate-determining steps of pathways I, II and III (1.68, 1.68 and 1.70 eV, respectively) are very close to each other. Since the transition state structures for the endothermic desorption of CH_2CO , H_2O , and CH_3OH cannot be found, the desorption free

Fig. 9. Schematic of the four pathways for direct syngas conversion.

energies (ΔG) are used as the reaction barriers and are compared to the G_a of the surface reactions; this overestimates the kinetics of the desorption steps. Moreover, the partial pressure of the reactants and products can also affect the rates of adsorption, desorption, and surface reactions in the Eley-Rideal mechanism. Therefore, to comprehensively evaluate the reaction activity, the rate constants at 673 K under 2.5 MPa of syngas with a H_2/CO ratio of 1.5 for all the elementary steps, including surface reactions, adsorption, and desorption were calculated and are presented in Tables S3–6. Table 1 lists the elementary steps that have a forward rate constant of $<10^3 \text{ s}^{-1}$ in the four pathways. Using the rate constant of 1.0 s^{-1} as a benchmark to evaluate the reactivity of the elementary steps on the active sites [68], pathways I, II and III are promising, whereas pathway IV is difficult due to its low forward rate constant of $2.48 \times 10^{-2} \text{ s}^{-1}$. Notably, pathway II for the formation of ketene is dominant as it is nearly 5 times faster than pathway I and 7 times faster than pathway III.

3.3. Discussion of the tendency to form ketene on FLPs

In pathway II, the C–C coupling can occur easily between two chemically adsorbed CO^* with a small G_a of 0.28 eV, which is attributed to the existence of the bent CO_2^{2-} active intermediate shown in Fig. 4. In pathway I, the C–C coupling between

Table 1

Rate constants (k_f and k_r) at 673 K for the selected elementary steps. ^a

Elementary steps	$k_f (\text{s}^{-1})$	$k_r (\text{s}^{-1})$
Pathway I: $2\text{CO}_{(\text{g})} + 2\text{H}_2 \leftrightarrow \text{CH}_2\text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$		
$\text{CH}_2\text{CO}^* + \text{OH}^* + \text{H}^* \rightarrow \text{CH}_2\text{CO}^* + \text{OH}^* + \text{H}^*$ (A13 → A14)	3.68	8.29×10^{-2}
$\text{CH}_2\text{CO}^* + \text{OH}^* + \text{H}^* \rightarrow \text{CH}_2\text{CO}_{(\text{g})} + \text{OH}^* + \text{H}^*$ (A14 → A15)	2.40×10^1	9.80×10^8
$\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}_{(\text{g})}$ (A17 → A18)	5.09×10^2	1.50×10^9
Pathway II: $2\text{CO}_{(\text{g})} + 2\text{H}_2 \leftrightarrow \text{CH}_2\text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$		
$\text{OCCHOH}^* + \text{H}_2(\text{g}) \rightarrow \text{OCHCH}^* + \text{H}_2\text{O}^*$ (B11 → B12)	1.74×10^1	8.30×10^6
$\text{CH}_2\text{CO}^* \rightarrow \text{CH}_2\text{CO}_{(\text{g})}$ (B15 → B16)	2.38×10^2	9.80×10^8
Pathway III: $\text{CO}_{(\text{g})} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})}$		
$\text{CH}_2\text{O}^* + 2\text{H}^* \rightarrow \text{CH}_2\text{OH}^* + \text{H}^*$ (C8 → C9)	2.61	2.17×10^3
$\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}_{(\text{g})}$ (C12 → C13)	6.99×10^1	2.25×10^9
Pathway IV: $\text{CO}_{(\text{g})} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}_{(\text{g})}$		
$\text{CO}^* + \text{H}_2^* \rightarrow \text{CHOH}^*$ (D2 → D3)	2.48×10^{-2}	3.23×10^5
$\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}^* + \text{H}^*$ (D7 → D8)	1.23×10^1	9.75×10^1
$\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}_{(\text{g})}$ (D8 → D9)	4.97	2.25×10^9

^a k_f and k_r are the forward and reverse rate constants, respectively. Steps with k_f less than 10^3 s^{-1} are displayed. $P(\text{H}_2) = 1.50 \text{ MPa}$, $P(\text{CO}) = 1.00 \text{ MPa}$, $P(\text{CH}_2\text{CO}) = P(\text{H}_2\text{O}) = 0.05 \text{ MPa}$, $P(\text{CH}_3\text{OH}) = 0.10 \text{ MPa}$.

Fig. 10. (a) Negative pCOHP curves for the C–O bonds and PDOS for the C atom in CHO* of state A4 in pathway I. (b) Negative pCOHP curves for the C–O bonds and PDOS for the C atom in CH₂O* of state C6 in pathway III. The Fermi levels of the CeO₂ slabs are set to zero in this figure.

CHO* and CHOH* also has a moderate G_a of 0.84 eV, suggesting the reactivity of CHO*. In Fig. 10(a), the electronic structure analysis of the CHO* actually forming a HCOO group with the O atom of FLPs is presented. The presence of the HCOO group (formate species) has been previously confirmed by *in situ* FT-IR studies of syngas conversion over the ZnO-ZrO₂ catalyst [13]. The pCOHP curves of the C–O bonds show that the unoccupied antibonding orbitals are close to the Fermi level. The projected density of states (PDOS) of C 2p shows a large contribution of the C atom to the antibonding orbitals that is indicative of a tendency of the C atom in CHO* to accept electrons. The rate-determining step in pathway III is the hydrogenation of CH₂O* with a large G_a of 1.70 eV, suggesting the stability of CH₂O*. Fig. 10(b) shows that no large peaks are observed close to the Fermi level in both pCOHP and PDOS of CH₂O*, indicating that the activation of CH₂O* is more difficult than that of CHO*. Similarly, CH₂O* binds with the surface O atom of FLPs to form an OCH₂O group in which the C atom is located at the center of the tetrahedron constituted by the four atoms in the OCH₂O group. Both electronic structure and geometric structure reflect the stability of CH₂O* on the reduced CeO₂(110) surface. Even though the H atom can first bind with an O atom to break the stable structure and then easily move to the C atom to form CH₃O*, our calculations show that the hydrogenation step is still challenging. Overall, the C atoms in CO*, CHO* and CH₂O* on FLPs all bind with two O atoms, one from CO molecule itself and another from the CeO₂(110) surface. Moreover, the C atoms in the former two are unsaturated while the C atom in the latter is saturated. Therefore, the easier C–C coupling of CO* or CHO* compared to the hydrogenation of CH₂O* is the underlying reason for the preferential formation of ketene on the FLPs of reduced metal oxides.

In addition, previous studies have proposed that CO is first activated through a disproportionation reaction to CO₂ and adsorbed C, *i.e.*, the Boudouard reaction, followed by a combination between the CH₂ species (originating from the hydrogenation of the adsorbed C) and CO to generate CH₂CO [9,11]. This mechanism is supported by the formation of CO₂ during the interaction of CO with metal oxides such as ZrCrO_x and MnO [9,11]. In our mechanism at the FLP sites on the reduced

CeO₂(110) surface, only water is produced together with ketene. However, the water produced in syngas conversion can react with CO to form CO₂ via a water gas shift reaction. In addition, after the formation of ketene through the C–C coupling of CO* or CHO*, CO can react with the surface O atom to generate CO₂, similar to the removal of the O atom by water production. Therefore, our proposed mechanism can also explain the formation of CO₂ during the generation of ketene over ZrCrO_x and MnO.

4. Conclusions

In this study, we investigated the role of reduced metal oxides, and particularly the frustrated Lewis pairs, in syngas conversion to ketene/methanol, the key intermediate step in the conversion of syngas to olefins via OX-ZEO catalysis. The main conclusions are as follows. (1) The frustrated Lewis pairs constructed via the oxygen vacancies of the metal oxide play a key role in syngas (H₂ and CO) activation. The H₂ is activated via a heterolytic dissociative pathway forming a hydride and a proton, and CO is activated in the form of CO₂²⁻ by combining with the basic site (O atom) of the FLPs. The hydride stabilized at the FLP site is the critical active species for the hydrogenation of CO. (2) Four pathways for the conversion of syngas were explored on FLPs, with two pathways for the formation of ketene and two pathways for the production of methanol. Rate constant calculations showed that the predominant route is the formation of ketene via pathway II which is attributed to the easier C–C coupling of CO* or CHO* compared to the hydrogenation of CH₂O*. Moreover, the neighboring FLP sites were also found to play a crucial role in the surface C–C coupling to produce ketene. Overall, our study provides novel insights into the role of oxygen vacancies in metal oxides and the reaction mechanism of syngas conversion over OX-ZEO catalysts.

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The calculations were performed by using the HPC Platform at Xi'an Jiaotong University and National Supercomputing Center in Guangzhou.

Graphical Abstract

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Role of surface frustrated Lewis pairs on reduced CeO₂(110) in direct conversion of syngas

Zheng-Qing Huang, Teng-Hao Li, Bolun Yang, Chun-Ran Chang*
Xi'an Jiaotong University

The frustrated Lewis pairs constructed via oxygen vacancies of metal oxides play a key role in activating syngas (H₂ and CO) and forming key intermediates (ketene and methanol).

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CeO₂(110)还原表面上受阻路易斯酸碱对在合成气直接转化中的作用

黄正清, 李腾昊, 杨伯伦, 常春然*

西安交通大学化学工程与技术学院, 陕西省能源化工过程强化重点实验室, 陕西西安710049

摘要: 随着石油资源的日益枯竭, 寻找非石油路线生产低碳烯烃的新途径显得十分重要。将天然气、煤以及生物质等经合成气(H₂和CO)转化为低碳烯烃是一条具有前景的路线。近年来, 双功能氧化物-分子筛(OX-ZEO)催化剂催化合成气直接制备低碳烯烃引起了国内外的广泛关注。由于CO活化并生成中间物种与C-C偶联分别在氧化物和分子筛上发生, OX-ZEO过程突破了费托合成中ASF产物分布的限制, 低碳烯烃选择性显著提高。虽然实验方面已经取得了大量进展, 但是OX-ZEO过程仍然存在一些关键问题, 特别是金属氧化物中氧空位的作用, 以及关键中间体是乙烯酮或甲醇的反应机理仍然不清楚。因此, 本文通过密度泛函理论(DFT)计算来解决上述两个问题, 对典型的可还原金属氧化物CeO₂表面上的合成气直接转化进行了理论研究。

计算结果表明, CeO₂(110)表面上的氧空位通过形成受阻路易斯酸碱对(FLP), 在活化H₂和CO中起着关键作用。H₂在FLPs上经过异裂分解, 形成与O原子结合的质子以及Ce原子结合的氢负离子, 其反应活化能仅为0.01 eV, 并且稳定在FLP位点的氢负离子将是CO加氢的关键活性物种。在FLP上, CO通过与FLP的碱性位点(O原子)结合形成CO₂²⁻实现活化, 其吸附能为-1.68 eV。随后, 我们在FLP上探索了四种合成气的转化途径, 其中两种容易形成乙烯酮, 另外两种倾向于产生甲醇, 该结果恰好可以解释实验上关于此两种中间产物的报道。通过计算反应条件下的反应速率常数, 我们对四条反应路径进行了比较, 发现从两个CO*经过表面C-C偶联形成OCCO*, 并最终形成乙烯酮是最占优势的反应路径, 并且在FLPs位点上CO*或CHO*的C-C偶联比CH₂O*的加氢更容易发生。此外, 我们发现相邻的双FLP位点在表面C-C偶联形成乙烯酮反应中至关重要, 主要由于相邻的双FLP位点可以使CO*或CHO*同时吸附, 因而有助于表面C-C偶联发生。总之, 本文首次揭示了表面FLP或氧空位在活化H₂和CO中的作用, 以及形成乙烯酮或甲醇的反应机理, 从而为OX-ZEO催化剂催化合成气直接转化提供了机理认识。

关键词: 合成气转化; 低碳烯烃; 氧化物-分子筛; 受阻路易斯酸碱对; CeO₂

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*通讯联系人. 电子信箱: changcr@mail.xjtu.edu.cn

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