



Direct conversion of methanol to ethanol on the metal-carbon interface

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Abstract: Direct conversion of one-carbon (C1) compounds to two-carbon (C2) and multi-carbon compounds remains a critical challenge for converting non-petroleum resources to valuable chemicals or fuels. The key issue is the selective activation of C1 compounds, methanol, as well as the controlled formation of carbon-carbon (C-C) bonds. Herein, we achieve the direct electrocatalytic methanol to ethanol, an important chemical and energy candidate, with methanol conversion, ethanol selectivity, and faradic efficiency of 257.0 g m⁻² h⁻¹, 95.1 %, and 12.45 %, respectively. Furthermore, the appropriate participation of water, as a by-product from methanol electrocatalysis, in hydrogen evolution reaction (HER) facilitates electrocatalytic reaction of methanol. Mechanistic studies reveal hydroxymethyl and methyl radicals are formed on the electropositive low-valent metal sites and electronegative carbon vacancies, respectively, and then combined with each other to form ethanol at the metal/carbon interface. This work opens a unique route for high-efficient concerted redox conversion of methanol reactant to ethanol.

With the exhaustion of petroleum resource, the utilization of non-petroleum carbon resources offers an alternative strategy to produce important petro-chemicals and fuels.^[1] Methanol, as an abundant and renewable C1 resource, can be obtained from carbon dioxide and biomass,^[2] as well as natural gas and coal,^[3] which has generally been used to synthesize C₂₊ hydrocarbon and oxygenates.^[4] Among them, selective and direct methanol coupling to C2 compound, ethanol, has become extremely attractive in catalytic chemistry for both academia and industry.^[5] It's accepted that the oxygen-hydrogen (O–H) dissociation in methanol is the more favorable than the carbon-hydrogen (C–H) and carbon-oxygen (C–O) bond scissions. As a result, ethanol has generally been synthesized from methanol via a carbonylation reaction followed by a reduction process.^[6] Recently, Wang's group studied the cleavage of C–H bond in methanol into ethylene glycol on photoexcited holes on CdS. Additionally, Jiang's group found the ratio of C–O/C–H dissociation in methol can enhance by 100 times through exciting the C–O stretching mode using a linearly polarized laser technology. Moreover, Wang's group found that ethanol with an selectivity of 65.0 % can achieve from methanol homologation using

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a $[RuCl_2(CO)_3]_2/Co_4(CO)_{12}$ bimetallic catalyst in lower reaction temperature, 160 °C,. ^[5] However, direct concerted dissociation of C–H and C–O bond in methanol to ethanol still remains a great challenge.^[7]

Metallic cobalt is a conventional catalyst for C-C coupling reactions. It has the advantages of the high catalytic activity and high selectivity of C₂₊ hydrocarbons and oxygenates through crystallite size or surface composition.^[8] To date, concerns over mild catalytic conditions have recently been concentrated on electrocatalysis process, such as HER of water, CO₂ reduction and ammonia synthesis (NRR). The controlled electrocatalytic features of a metal and carbon composite result in an extraordinary synergistic effect between the electropositive metallic species and electronegative carbon support. On the electrocatalytic material, the carbon vacancies with the higher electronic density could facilitate electroreduction reactions, such as the oxygen reduction reaction (ORR) and HER reactions. In the meanwhile, the electropositive metal species could adsorb hydroxyl to facilitate the electrooxidation reaction, such as the oxygen evolution reaction (OER).^[9] The field generated by this ion-image-charge pair in the electrode also interplays with polar adsorbates at a longer range to even control the kinetics of electrochemical reactions.^[10] When Co and carbon species are present on either side of an interface of catalysts simultaneously, concerted redox conversion of methanol may proceed to provide an opportunity to increase ethanol selectivity on catalysts.

Herein, we demonstrate a direct electrocatalytic route from methanol to ethanol with high selectivity at 20 °C and atmospheric pressure. There is three remarkable characteristics in this reaction: (1) the specific adsorption of methanol on the surface of the electrocatalyst; (2) the controllable cleavage of C-H and C-O bonds at neighbouring metal-carbon active sites of the electrocatalyst; (3) the tailorable participation of by-product water from electrocatalytic reaction of methanol, in HER, which facilitates the formation of C-C bonds. In brief, a synergetic mechanism was proposed for the direct electrocatalytic conversion of methanol to ethanol on a unique ^[111] electrocatalyst. Because of the localized charge distribution at the metal/carbon support interface under an electric field,^[12] the low-valent Co sites are electropositive and the adjacent carbon vacancies are electronegative. Consequently, the different dissociation mechanisms of methanol on this electrocatalyst occur to form hydroxymethyl and methyl radicals on neighbouring metal and carbon active sites, respectively. The C-C coupling between hydroxymethyl and methyl adsorbates produces ethanol at the interface. A higher ethanol selectivity 95.1 % at 20°C is achieved with methanol conversion of 257.0 g m⁻² h⁻¹ and faradic efficiency of 12.5 % than conventional methanol homologation with an ethanol selectivity of 65.0 % in 160 °C ^[5]. The overall reaction can be expressed as equation (1).

$$2CH_3OH \rightarrow CH_3CH_2OH + H_2 + 1/2O_2 \tag{1}$$

It should be noted that the conversion of methanol to ethanol according to equation (1) cannot occur at temperatures lower than 500 $^{\circ}$ C based on thermodynamic calculations (Figure S1). Electrocatalysis provides

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a potential strategy to convert methanol to ethanol under ambient conditions. In principle, the driving force of electrocatalysis is the interfacial or surface potential. Under certain potentials, the activations of both C-H and C-O bond would become possible following methanol adsorption on the surface of the electrocatalyst.^[5,13] We performed electrocatalytic conversion of methanol using a series of carbon-supported Ni, Ru, Rh, Co, and Co₃ZnC catalysts, as listed in Table 1. Fascinatingly, Co₃ZnC/NC shows better catalytic performance for direct conversion of methanol to ethanol than the others. Its performance is even higher than that of the noble metal catalysts with similar metal loading. The Co₃ZnC/NC catalyst presents a methanol conversion of 203.2 g m⁻² h⁻¹, and an ethanol selectivity of 93.1 % (GC-MS and GC analysis of products in liquid and gas phase are shown in Figures S2 and S3, respectively).

Table 1. Comparison of methanol conversion and products selectivity over different catalysts^[a]

Entry	Catalyst	Conversion ^[b] Selectivity ^[c] (%)			EtOH yield	
		$(g m^{-2} h^{-1})$	EtOH	Dimethyl ether ^[d]	Ethylene glycol ^[d]	$(g m^{-2} h^{-1})$
1	10% Ni/ZIF-8-C	68.6	79.9	18.3	2.8	39.5
2	5%Ru-RuO ₂ /BP2000 ^[e]	89.6	97.0	1.9	1.1	62.5
3	5% Rh/C ^[e]	125.4	97.7	1.4	0.9	88.0
4	10% Co/BP2000	83.7	76.4	18.2	5.4	46.0
5	10% Co ₃ ZnC/NC	203.2	93.1	5.6	1.3	136.0

[a] Reaction performances were evaluated under catalyst loading of 12.5 ± 0.187 , 25 ± 0.285 , 25 ± 0.310 , 12.5 ± 0.206 , $12.5 \pm 0.135 \text{ mg/cm}^2$ for 10% Ni/ZIF-8-C, 5% Ru-RuO₂/BP2000, 5% Rh/C, 10% Co/BP2000 and 10% Co₃ZnC/NC, respectively. The corresponding change of potentials was presented in Figure S4 in electrocatalytic reaction process. And the experiments were repeated for three times. [b] Methanol conversion was calculated based on the electrode area and reaction time. [c] Selectivity was obtained on a molar carbon basis. [d] Dimethyl ether and ethylene glycol were denoted as DME and EG, respectively. [e] The 25 mg/cm² catalyst was used to maintain the same metal loading as the other catalysts. The ratio between Ru and RuO₂ in 5% Ru-RuO₂/BP2000 is about 0.11.

By using Co₃ZnC/NC, the effects of reaction conditions on the catalytic performance, including temperature, potential, current, time, electrolyte pH value, stirring speed, and the catalyst amount, were investigated (Figure S5). The optimal operation parameters are the reaction temperature of 30 °C, the current of 10 mA/cm², 4.5 h, pH of electrolyte solution of 11.5, stirring speed of 600 rpm, and 12.5 mg/cm² loading of the catalysts. We discovered that, under this optimized condition, the methanol reaction rate and ethanol selectivity are 257.0 g m⁻² h⁻¹ and 95.1 %, respectively. These are accompanied by the generation of

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hydrogen^[14] and an increase in the solution pH in the cathodic chamber, as well as oxygen evolution in the anodic chamber according to equation (2) and (3). The half-reactions occurred in cathodic and anodic chambers are expressed as followed:

Cathode:
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
 (2)

$$4\text{MeOH} + 2e^- \rightarrow 20H^- + H_2 + 2EtOH \tag{3}$$

Anode:
$$2H_2 0 \to 0_2 + 4e^- + 4H^+$$
 (4)

The catalytic behavior of Co₃ZnC/NC depends on its specific redox property (unpassivated, reduced or oxidized form, Table S1). 10 % Co₃ZnC/NC exhibited the best electrocatalytic performance for direct methanol conversion among all the samples with different calcination pretreatments. Thus, these Co₃ZnC/N-based samples were used to further study the structure-property relationships.

To explain the nature of the crystal phases, X-ray diffraction (XRD) patterns of the samples are presented in Figure S6. The reduced, unpassivated, and oxidized Co₃ZnC catalysts exhibit an obvious diffraction peak at 41.9 °attributed to the (111) lattice of cubic Co₃ZnC, and another peak at 47.6 °corresponding to the (101) lattice of hexagonal Co, as well as individual redox characteristic peaks. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive spectroscopy (EDS) elemental mapping were employed to determine the positions of elements, the composition, and the particle size of the unpassivated Co₃ZnC/NC catalyst. As shown in Figure 1a and b, Co, Zn, and C are uniformly distributed and overlap with each other, indicating the presence of the Co₃ZnC phase. The (111) interplanar spacing of 0.216, corresponding to Co₃ZnC, was also observed in the high-resolution TEM (HRTEM) micrograph (Figure 1c). Additionally, the particle size of the Co₃ZnC/NC was obtained by the Scherrer equation to be 11.4 nm (Table S2), which is similar to the result from TEM in Figure 1d. In addition, we analyzed the composition of the surface elements over Co₃ZnC/NC catalysts using X-ray photoelectron spectroscopy (XPS). The results are presented in Figure S7 and Tables S3 and S4. The Co₃ZnC/NC catalyst contains a certain amount of low-valent Co species, attributed to Co3ZnC and Co metal. The amount of lowvalent Co species decreases in the following sequence: reduced Co₃ZnC/NC>unpassivated Co₃ZnC/NC>oxidized Co₃ZnC/NC (Table S3). And for the XPS spectra of C 1s, Co₃ZnC/NC presents the higher ratio at 284.4 eV, assigned to metal carbide, which is partially related to the interaction of Co₃ZnC with the carbon support (Table S4). By combining the XRD, TEM and XPS results, it is clear that the nanoparticles of cubic Co₃ZnC and Co are uniformly dispersed on the surface of the carbon support.

The signal centered at 2.0043 for the unpaired electrons indicates the appearance of carbon or zinc vacancies in Figure 1e.^[16] By comparison, the ZIF-8-C support shows a relatively weak characteristic signal, while Co₃ZnC/NC has the highest among all the samples. The formation of more carbon vacancies on the

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catalysts is related to the addition of the cobalt precursor and the generation of the low-valent Co_3ZnC and Co crystal phase. Additionally, compared with the support ZIF-8-C, the intensity ratio of the D and G bands (I_D/I_G) decreases with the addition of Co in Figure 1f, implying interfacial contact between low-valent Co species



Figure 1. Composition of the Co₃ZnC/NC catalyst. a) HAADF-STEM image of the unpassivated Co₃ZnC/NC catalyst. b) Corresponding EDS maps with in the region marked by the red rectangle in the HAADF-STEM image. c) and d) HRTEM micrographs and the histogram of the particle size. e) Low-temperature ESR spectra of the catalysts. f) and g) Raman spectra of the catalysts.

and carbon vacancies.^[9] Through curve fitting with a Lorentzian function, the value of $I_D/I_{D'}$ is about 5.8 for Co_3ZnC/NC based catalysts (Figure 1g), which is higher than the value of 4.6 measured on the ZIF-8-O support, indicating that more carbon vacancies are formed over Co_3ZnC/NC catalysts^[17]. Importantly, these carbon vacancies are adjacent to low-valent Co species in the graphitization process of Co_3ZnC/NC . Combining the evaluation with characterization results, Co_3ZnC/NC , which simultaneously has more low-valent Co species and carbon vacancies on the support, illustrates excellent electrocatalytic performance (Table S5). Positive correlation between interface composition and electrocatalytic performance indicates that the synergy between Co_3ZnC or Co and carbon vacancies indeed dominates electrocatalytic performances for direct methanol to ethanol. The endurance test also indicates that the structures and compositions of

Co₃ZnC/NC change slightly during the methanol electrocatalysis process, leading to stable electrocatalytic performances of methanol (Figure S8 and Figure S9).

It is accepted that Co₃ZnC is a potential catalyst for HER in water. In this case, comparison of Tafel slopes, LSV curves, and electrocatalytic performance of HER from water and methanol conversion was accomplished to further understand the reaction mechanism, since water is also a possible by-product of the direct methanol to ethanol conversion as well as from water permeability by N117 membrane from anode compartment.

The Tafel slopes for pure methanol consumption and HER in a single-chamber reactor (SCR) are 86.5 and 114.6 mV dec⁻¹, respectively, and it is 62.9 mV dec⁻¹ under the conditions of the co-occurrence of methanol consumption and HER in a two-compartment reactor (TCR) in Figure 2a, indicating that under the certain potentials, actual methanol conversion is preferred in comparison with HER from water or individual methanol electrocatalysis over the Co₃ZnC/NC catalyst. The relative lower electrocatalytic performances for HER from water is partially related to hydrophobic properties of Co₃ZnC/NC (Figure 2b).^[18] On the other hand, as a byproduct from methanol electrocatalysis, water in HER also promotes methanol conversion to some extent. By comparison with 58.6 g m⁻² h⁻¹ in a SCR, methanol conversion is 203.2 g m⁻² h⁻¹ in a TCR. The LSV for methanol electrocatalysis in a TCR (Figure 2c) also shows increased electroreduction current in TCR compared with that in a SCR. The tailorable participation of by-product water from direct methanol electrocatalysis in HER enhances the occurrence of electrocatalysis of methanol in TCR. However, the addition of excess water can affect the ethanol yield due to the dilution of reactant methanol.



Figure 2. Electrocatalytic performance of Co₃ZnC/NC catalyst in methanol and H₂O. a) Tafel slopes. b) Contact angles. c) LSV curves.

To further examine the reaction mechanism, we investigated the possible radicals generated during the electrocatalysis process using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin-trapping agent^[5] (Table S6). With the addition of DMPO, the formation of ethanol is evidently suppressed, implying that ethanol is

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generated via free radical intermediates. Electron spin resonance (ESR) spin trapping is widely used to detect short-lived free radicals, since ESR is sensitive to a relatively stable paramagnetic nitroxide adduct, formed by spin traps, DMPO and active free radicals^[19]. Therefore, in situ ESR spectroscopic study in the presence of DMPO was employed to detect the generation of the hydroxymethyl radical (\cdot CH₂OH) and methyl radical (\cdot CH₃) during the reaction process by comparing the results with and without electricity supply. We observe DMPO-CH₂OH (a_N=15.7, a_H=21.5) and DMPO-CH₃ (a_N=16.0, a_H=22.3) signals during the electrocatalytic reaction (Figure 3). This means that methyl and hydroxymethyl coexist during the electrocatalytic process. In the absence of a spin-trapping agent, the formed hydroxymethyl and methyl radicals might freely collide with one another to generate ethanol, ethylene glycol, or ethane products. Fascinatingly, the selectivity of ethanolis 95.1% for electrochemical conversion. In contrast, the selectivities for other products, such as dimethyl ether and ethylene glycol, are negligible.

As mentioned above, the synergy from low-valent Co species adjacent to carbon vacancies is a critical factor for methanol electrocatalysis. More importantly, these species on the interface might serve as active sites for hydroxymethyl and methyl formation,^[20] respectively. Once these radicals are generated, they subsequently migrate and combine to form the product ethanol over the surface of catalysts in Figure 4. The appropriate participation of water in HER facilitates electrocatalytic conversion of methanol, because water acts as a by-product in methanol electrocatalysis process. Meanwhile, this participation also enhances the electrolyte solution pH to contribute to further methanol consumption. As aforementioned, higher pH favors methanol electrocatalysis.



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Figure 3. In situ ESR spectra of electrocatalytic reaction systems in TCR in the presence of DMPO with or without electricity. a) Electrochemical reaction conditions were a N₂-saturated solution of 0.147 g NaCl in 25 mL methanol containing Co_3ZnC/NC catalyst with DMPO (cathode chamber) and that of 25 mL 0.5 M aqueous Na₂SO₄ (anode chamber). Characterization conditions were microwave frequency of 9.44 GHz, microwave power of 20 mW, modulation frequency of 100.00 kHz; b) Reaction and characterization conditions were consistent with a)except for no addition of electricity; c) Related conditions were consistent with **b** except for no addition of DMPO in cathode chamber.



Figure 4. Schematic illustration of Co_3ZnC/NC catalyst for direct electrocatalytic conversion of methanol to ethanol and the plausible reaction mechanism.

We also conducted control experiments without water or the electrolyte, NaCl, in SCR (Figure S10) for in-depth understanding of the electrocatalysis mechanism in TCR. In situ ESR signals for the CH₂OH radical in TCR (Figure 3) are 2.4 fold higher than those without water in SCR (Figure S10a), indicating the electrocatalytic capacity increases with the addition of a certain amount of water. Moreover, ESR spectra for DMPO-CH₃ disappear without NaCl and water in SCR (Figure S10b). Thus, the more prominent ESR signals corresponding to high electrocatalytic performance in TCR confirm that methanol electrocatalysis to ethanol is promoted by the optimized electron polarization of the catalysts induced by an electric field.

In summary, direct methanol electrocatalysis into ethanol with high efficiency was achieved in this work. An excellent ethanol selectivity of 95.1 %, a yield of 175.6 g·m⁻²·h⁻¹ and faradic efficiency 12.5 % were obtained under the optimal reaction conditions. The tailorable participation of water in HER contributes to methanol consumption in the electrocatalytic process. Control DMPO experiments and the corresponding ESR confirm the generation of methyl and hydroxymethyl during the electrocatalytic process. The synergy between electropositive low-valent Co species and adjacent electronegative carbon vacancies facilitates the formation of hydroxymethyl radical and methyl on Co_3ZnC/NC , respectively, which further react to generate ethanol. This work paves a path for an amazing promotion of catalytic efficiency by electrocatalytic redox conversion of methanol reactant as well as a highly efficient, nonpetroleum route for the synthesis of ethanol.

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Conflict of interest

The authors declare no competing interests.

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