Communication

Room-temperature conversion of ethane and the mechanism understanding over single iron atoms confined in graphene

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\section*{A B S T R A C T}

The catalytic conversion of ethane to high value-added chemicals is significantly important for utilization of hydrocarbon resources. However, it is a great challenge due to the typically required high temperature (≥ 400 °C) conditions. Herein, a highly active catalytic conversion process of ethane at room temperature (25 °C) is reported on single iron atoms confined in graphene via the porphyrin-like N\textsubscript{4}-coordination structures. Combining with the operando time of flight mass spectrometer and density functional theory calculations, the reaction is identified as a radical mechanism, in which the C–H bonds of the same C atom are preferentially and sequentially activated, generating the value-added C\textsubscript{2} chemicals, simultaneously avoiding the over-oxidation of the products to CO\textsubscript{2}. The in-situ formed O–FeN\textsubscript{4}–O structure at the single iron atom serves as the active center for the reaction and facilitates the formation of ethyl radicals. This work deepens the understanding of alkane C–H activation on the FeN\textsubscript{4} center and provides the reference in development of efficient catalyst for selective oxidation of light alkane.

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Dehui Deng’s Group for Two-dimensional (2D) Materials & Energy Catalysis. Our research focuses on the development of 2D material-based catalyst and their applications in catalytic conversion of energy molecules, mainly including: (1) Designing and synthesis of advanced 2D materials and their heterostructures, such as graphene, MoS\textsubscript{2}, LDHs, for efficient catalytic activities. (2) Thermochemical, electrochemical and thermo-electrical coupled catalysis toward highly efficient activation and conversion of energy molecules, such as O\textsubscript{2}, H\textsubscript{2}, H\textsubscript{2}O, CO, CO\textsubscript{2}, CH\textsubscript{4} and CH\textsubscript{4}OH. (3) Computational and theoretical modeling of energy catalysis systems to provide fundamental understandings of catalytic activation and reaction mechanism for catalyst optimization and development.

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Ethane as one abundant component of natural gas, shale gas and combustible ice, the exploitation has been in rapid growth in recent years [1]. The value-added C\textsubscript{2} chemicals converted from ethane, such as ethanol, acetic acid and ethene, are widely used as fuels, plastic building block, chemical feedstock [2–6], thus the catalytic conversion of ethane is an important process. However, the high bond energy of C–H (409 kJ/mol) makes the process extremely difficult. High temperature (≥ 400 °C) [7–9] conditions are typically required in the conventional industrial process, which usually brings side-effects such as over-oxidation of the products and carbon deposition on the catalyst.

Recently, it was reported that ethane can be partially oxidized by H\textsubscript{2}O\textsubscript{2} in strong acidic medium at 50–180 °C using complexes with metal cores of V, Mn, Fe, Mo, Ru, Pd, Os, and Pt as homogeneous catalysts [10–14]. In addition, the Fe or Cu modified zeolite catalysts exhibited superior performance in ethane partial oxidation at 50 °C using H\textsubscript{2}O\textsubscript{2} as oxidant in heterogeneous catalysts.

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The excessive H$_2$O$_2$ might break some of FeN$_4$ active centers, causing the decreasing of conversion (Fig. S1), and therefore a moderate H$_2$O$_2$ concentration was used in this study. The reaction products are analyzed by NMR, TOF-MS and gas chromatography (GC). The catalytic activity of various MN$_4$/GN samples is presented in Fig. 1(b). As shown in Fig. 1(b), FeN$_4$/GN exhibits the optimum activity for ethane oxidation compared with other metal centers according to the amounts of products and turnover number (TON). The GC characterization results confirm the generation of C$_2$H$_4$ in gas phase and the absence of over-oxidized products (CO$_2$) (Fig. S4). After carefully analyzing the liquid products by various characterization techniques including the $^{1}$H NMR (Fig. S5), $^{13}$C DEPT-135 (distortionless enhancement by polarization transfer) (Fig. 1c), $^{13}$C NMR (Fig. 1c), and HSQC-NMR (heteronuclear single quantum coherence) (Fig. S6), we found that the ethane can be transformed to C$_2$ components, i.e. the CH$_3$CH(OH)$_2$, CH$_3$COOH, CH$_3$CH(OH)$_2$ and CH$_3$CH$_2$OH at room temperature [15]. Moreover, the structure of these products was also confirmed by the TOF-MS (Fig. 1d). The peaks of CH$_3$COOH and CH$_3$CH$_2$OH can be easily marked. However, the signals of CH$_3$CH(OH)$_2$ and CH$_3$CH$_2$OH are overlapped due to the same molecular weight. These results are consistent with the NMR data. In addition, considering the catalyst itself contains the carbon sources, we also carried out the contrast test under the N$_2$ condition (Fig. S7), while the C$_2$ products were not observed in the $^{1}$H NMR data. It illustrates that the C$_2$ components come from the ethane rather than the catalyst itself. In addition, the stability tests reveal that the FeN$_4$/GN can keep the 60% catalytic activity after six cycles, demonstrating its good stability (Fig. S8).

Furthermore, we used the operando TOF-MS to track the reaction process over the FeN$_4$/GN sample (Fig. S9). The liquid phase
products can be analyzed by TOF-MS in real time through the filter and capillary under the high pressure (typically 1.6 MPa). The increasing rate of different products can be observed during the reaction (Fig. 2a), which were further analyzed towards the increasing rate of the products in the first 300 min and last 300 min (Fig. 2b). The increasing rate of CH₃CH₂OOH, CH₃CH(OH)₂ and CH₃CH₂OH in the first 300 min is greater than in the last 300 min. On the other hand, most of CH₃COOH is produced in the last 300 min. Besides, the similar results were also observed under the different pressures (0.8 MPa, 1.2 MPa) in the operando TOF-MS studies (Fig. S10). These results suggest that ethane should be initially converted to CH₃CH₂OH and CH₃CH₂OOH via oxidation of single C–H bond of ethane followed by further oxidation of these products, leading to the formation of CH₃COOH and CH₃CH(OH)₂. To confirm this hypothesis, we directly used ethanol as the reactant and obtained the CH₃COOH and CH₃CH(OH)₂ (Figs. 2c and S11), which indicates that the ethane can be converted into CH₃COOH and CH₃CH(OH)₂ via ethanol. Besides, controlling the reaction time, it can be observed that the selectivity of CH₃CH₂OOH and CH₃CH₂OH decreases and the selectivity of CH₃COOH and CH₃CH(OH)₂ increases during the reaction, which suggests that CH₃COOH and CH₃CH(OH)₂ may come from CH₃CH₂OOH and CH₃CH₂OH (Fig. S12). According to the above experimental results, we propose one possible reaction route (Fig. 2d). The ethane is firstly converted to the CH₃CH₂OOH and CH₃CH₂OH. The generated CH₃CH₂OH will be further oxidized to CH₃CHOH, and CH₃COOH. And the CH₃CH₂OOH can also be converted to CH₃COOH.

DFT calculations were carried out to further understand the ethane conversion process. A model of FeN₄ structure confined in the matrix of graphene with the central Fe atom coordinated with four N atoms has been built to simulate the FeN₄/GN catalysts. In the aqueous H₂O₂ environment, FeN₄ is easy to adsorb two O atoms and form the O–FeN₄–O structure (Fig. 3a), which is the active site for C–H bond cleavage [21,23]. The structure of O–FeN₄–O has been proved by X-ray absorption fine structure spectroscopy (XAFS) and Mössbauer spectra in our previous work [21]. The ethane activation is along a radical mechanism. As shown in Fig. S13, the C–H bond of C₂H₆ is stretched on the O–FeN₄–O site, through a transition state (TS) forming a -CH₂CH₃ radical, which will bind with the OH group on the surface to generate CH₃CH₂OH, and the left FeN₄–O structure will react with the H₂O₂ in the solution to cycle back to the O–FeN₄–O active structure. The activation barrier is only 0.48 eV, which means the ethane activation can be performed in mild conditions (Fig. 3b). As shown in Fig. 3(a), the -CH₂CH₃ radical may also bind with one -OOH group in the H₂O₂ solution to form CH₃CH₂OOH or break another C–H bond to form CH₃CH₂.

The generated CH₃CH₂OH molecules can be further activated on the O–FeN₄–O site. As shown in Figs. S14 and S15, compared with the CH₃ group (barrier: 0.56 eV), the CH₂ group is more easily to be activated (barrier: 0.20 eV) to form CH₃CH(OH)₂ radical, which was confirmed by the electron paramagnetic resonance experiments (Figs. S16 and S17). The CH₃CH(OH)₂ radical can also be dehydrated to generate CH₃CHO. Moreover, the last C–H bond

Fig. 2. Mechanism study of FeN₄/GN for ethane conversion. (a) The operando TOF-MS data obtained from C₂H₆ oxidation. (b) The increase rate of the products at 0–600 min, which corresponds to the relative intensity increment. (c) ¹³C NMR result of CH₃CH₂OH oxidation by FeN₄/GN. (d) A possible reaction path for ethane oxidation over FeN₄/GN catalyst. Reaction conditions in (a): 50 mg catalyst, 10 mL H₂O₂ (15%) at 25 °C for 10 h; in (c): 50 mg catalyst, 10 mL H₂O₂ (15%), 0.03 M CH₃CH₂OH, 1.6 MPa N₂, in a steel autoclave with a Teflon inner vessel (100 mL) at 25 °C for 10 h.
on the C atom of CH$_3$CHO can be very easily activated (barrier: 0.02 eV) to form a further oxidation product CH$_3$COOH, which explains that almost no aldehyde products were detected. The DFT results agree well with the experimental results.

In conclusion, we report a FeN$_2$/GN catalyst with high activity for the conversion of ethane to C$_2$ chemicals at room temperature. Through a series of experiments including operando TOF-MS and DFT calculations, we found that the O–FeN$_2$–O structure formed in aqueous H$_2$O$_2$ is able to convert ethane to ethyl radical in mild conditions. The ethyl radicals will bind with the -OH and -OOH groups to form CH$_3$CH$_2$OH and CH$_3$CH$_2$OOH. Furthermore, through activating the C–H bonds on the same C atom, CH$_3$CH$_2$OH could be further converted to CH$_3$CH(OH)$_2$ and CH$_3$COOH. These findings provide the reference for understanding and designing highly efficient catalysts for C–H bond activation and conversion.

Acknowledgments

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Supplementary material

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