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DFT study on the active site of the monometric molybdenum anchored on silica for the selective oxidation of ethane to acetaldehyde

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ABSTRACT

One of the most intriguing questions regarding of Molybdenum catalysts in selective ethane oxidation to acetaldehyde is the true active center. Due to the multiple valence of Mo, it is not very straightforward to assign active site from the experimental observation. In this work, DFT calculations reveal that the absorbed oxygen molecule on the reduced Mo catalysts rather than Mo═O and Mo−O−Si in the original monometric Mo catalysts is the real active species to break C−H bond. Furthermore, the reactivity of adsorbed oxygen molecule is very sensitive to the Mo coordination at the adsorption site. The calculated reaction pathway and rate constant support the active site assignment. The conclusions further deep the understandings of Mo catalysts and contribute to the design of novel catalysts.

1. Introduction

The worldwide found Shale gas reservations not only change the energy landscape but also supply abundant short alkane molecules. Shale gas, a kind of nature gas, generally consists with 90% methane and 10% ethane/propane [1,2]. Therefore, the effective conversion of light alkane molecules to value-added chemicals will have a paramount importance for the exploit of the Shale gas resource. It is well known that the supported molybdenum oxide catalyst is very effective for the light alkane selective oxidation including methane, ethane, and propane [3–9]. The supported Mo catalysts on silica have been proposed to have very different structures which is depending on the catalyst loading, preparation method, and the nature of the support [10,11]. From the theoretical simulation pointview, the tetra-coordinated di-oxo and penta-coordinated mono-oxo Mo species are determined to be the most important structures which are shown in Fig. 1. Chempath et al. perform DFT on the free energy change for the conversion between di-oxo and mono-oxo Mo [12]. It is concluded that the di-oxo structure is more favourable. However, the mono-oxo structure is more favourable under the reduction which is supported by the agreement between the calculated and experimental observed EXAFS spectrum. Guo et al. carefully calibrate the geometry parameters of the tetrahedral, pentahedral, and octahedral coordinated Mo spices on silica support in a combined theoretical and experimental work [13]. They observed that the supported Mo catalysts have an excellent performance in oxidation dehydrogenation of propane to form propylene. The most likely active species is identified to be tetra-coordinated di-oxo structure which is also supported from the NXEFS spectrum calculation. However, the above mentioned DFT studies do not have a detailed discussion on the effect of silica support. Handzlik et al. use both periodic and cluster silica models in the calculation to study the structure of supported Mo catalysts [14]. The calculations reveal the location of Mo on silica support has a significant influence on the active species structure. For example, the mono-oxo structure become favorable if a 4-fold bonding on silica is provided. Overall, it is suggested that di-oxo Mo structure on silica support is more favourable from thermodynamics and spectrospy. Furthermore, experimentally it is indicated that the highly dispersed Mo on SBA-15 plays an important role in the oxidative conversion of ethane into acetaldehyde and ethylene [15]. The maximum yield of aldhydes reached 4.2% over Mo 0.75/SBA-15 catalyst at the reaction temperature of 625 °C. Results demonstrated that the low Mo content is beneficial to the formation of isolated tetra-coordination Mo species.

The correct understandings on the reaction mechanism is strongly dependent on the identification of structure of the active site. To reach an unambiguous determination of the active site on Mo catalysts, both isolated tetra-coordinated di-oxo and penta-coordinated mono-oxo structures are considered in current work. Furthermore, the

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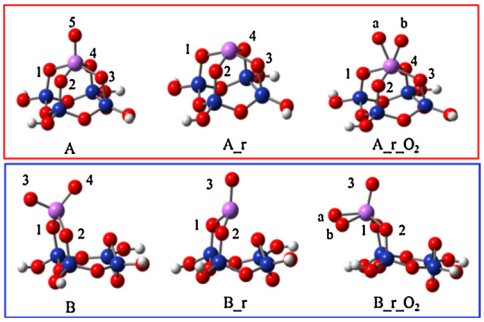

Fig. 1. The optimized structures of the isolated monometric molybdenum anchored on silica. The monooxo Mo(VI) and dioxo Mo(VI) species are indicated as A and B, respectively. The reduced monooxo Mo(IV) and dioxo Mo(IV) species are indicated as A_r and B_r, respectively. The optimized geometries after O_2 adsorption on the reduced monooxo Mo(VI) and dioxo Mo(VI) species are indicated as A_r_O_2 and B_r_O_2, respectively. 1–5 indicates the different oxygen in original catalysts and a,b indicates the adsorbed oxygen molecule. The oxygen is red color, Mo is purple, Silica is blue and white is hydrogen. The detailed geometry parameter are shown in Table S1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

calculations are performed for the reaction pathway, thermodynamics and rate constant for the selective oxidation of ethane to acetaldehyde on both two structure. In the end, a relation between structure of active species and the catalytic performance is established.

2. Results and discussion

The optimized structures of tetra-coordinated di-oxo (B) and penta-coordinated mono-oxo Mo (A) catalysts on silica are shown in Fig. 1 and the geometry parameters are listed in Table S1. The coordinated oxygen atoms for A and B are different. The four coordinated oxygens for Mo in structure A are from the support. In contrast, only two coordinated oxygens for Mo in structure B are from the silica. Furthermore, there are one terminal oxygen (oxygen 5 in top panel in Fig. 1) and two terminal oxygens (oxygen 3,4 in bottom panel in Fig. 1) in structure A and B respectively. To examine the reactivity of the oxygen species in A and B, the first C–H bond activation in propane molecule on Mo catalyst is examined. The calculations reveal that the C–H bond activation is very difficult to proceed on Mo catalysts either in structure A or structure B as the barrier is over 170 kJ/mol as shown in Fig. 2. Both terminal oxygen (Mo═O) and bridge oxygen (Mo-O-Si) between Mo and support are considered. This suggests that these sites are unlikely to be active towards C–H bond activation. On the other hand, Mo catalyst readily undergo reduction-oxiation under reaction condition. It has been suggested the oxygen actively exchanged with the catalysts and the real active spices is the peroxide after oxygen adsorption on reduce MoO_x [16]. Therefore, the structures of reduced Mo (A_r and

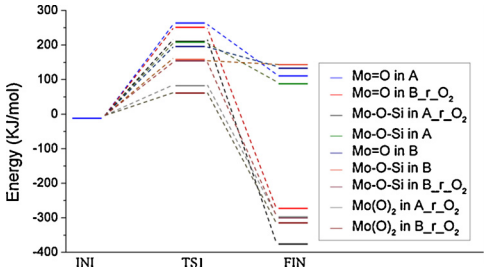

Fig. 2. The calculate reaction pathway of first C–H bond activation in ethane at various active sites on the Mo catalyst. The geometry of Mo = O, Mo-O-Si and $Mo(O)_2$ are indicated in Fig. 1. The structures along reaction pathway are shown in Figure S1.

B_r) and the subsequent oxygen molecule adsorption (A_r_O2 and B_r_O2) for A_r and B_r geometry are also obtained and shown in Fig. 1. The vibration of B, A, and B_r_O_2 is computed and shown in Table S3. The increase of Mo═O bond wavenumber after oxygen molecule adsorption is consistent with the experimental observation [17,18]. The binding energy of oxygen molecule on A_r and B_r is -144.7 and -148.5 KJ/mol respectively which indicate the strong interactions between oxygen molecule and reduced catalysts. After adsorption, the bond distance of oxygen molecule elongated be around 1.46 Å which is an indication of the peroxide oxygen formation. Furthermore, the first C—H bond activation of ethane is also investigated on the adsorbed oxygen ($Mo(O)_2$) as shown in Fig. 2. In contrast, The barrier is significantly reduced compared with Mo═O and Mo-O-Si sites in structure A and B. This clearly indicate the better catalytic performance of the adsorbed oxygen. The charge analysis shown in Table S2 indicates that the mechanism of C–H bond activation is different on Mo = O, Mo-O-Si and the adsorbed oxygen $Mo(O)_2$. At transition states, the hydrogen loses electrons and O, Mo are the charge acceptor at Mo═O and Mo—O—Si sites because oxygen mainly attacks hydrogen atom in ethane and forms surface hydroxyl and ethoxide as shown in Figure S1. On the other hand, the charge transfer happens between carbon and oxygen at the adsorbed oxygen sites in transitions states because oxygen attacks carbon in ethane to form the ethanol. Furthermore, the transition states (TS1) of the first hydrogen abstraction have different geometries at the different active sites as shown in Fig. 2 and Figure S1. TS1 on Mo catalysts in structure A and B is more like a later transition state as the breaking C—H bond distance is above 1.39 Å. In contrast, the breaking C—H bond distance in A_r_O2 and B_r_O2 is 1.22 and 1.23 Å respectively.

Moreover, the complete reaction pathway calculations are examined on the adsorbed oxygen site as shown in Fig. 3. The corresponding initial, transitional, intermediate and final structures along pathway are also indicated. The first step on the reaction pathway is the hydrogen abstraction from ethane molecule. The energy barrier is estimated to 94.3 and 72.8 KJ/mol on A_r_O2 and B_r_O2 respectively. Along the reaction pathway as shown in Fig. 3, one oxygen atom inserts into the C–H. After C–H bond breaking, and it reached a very stable intermediate, a weakly associated ethanol, which is downhilled by 285.5 and 302.8 KJ/mol for A_r_O2 and B_r_O2 respectively. The super stability of adsorbed ethanol also explains that the ethyl radical is not obtained by the DFT optimization. In the following the H atom in ethanol is abstracted by the another oxygen atom in peroxide oxygen which is corresponding to TS2 with a barrier of 117.1 and 113.0 KJ/mol. This step leads to the formation of a surface OH* and C_2H_5O* groups. The pathway continues that the H in the C_2H_5O* surface species transfers onto the OH* surface species to form weakly adsorbed water and acetaldehyde which is corresponding to TS3 with a barrier of 97.4 and 101.1 kJ/mol. In the end, acetaldehyde and water desorb from the surface which the desorption energies are shown in Table S4. Among three critical steps, the TS2 has the largest barrier which can be considered to be rate-limiting step. At the reaction temperature 898 K, the free energy barrier of rate-limiting step is much smaller on B_r_O2 than the counterpart on A_r_O2 as shown in Table 1. Furthermore, the calculated rate constant on B_r_O2 is three magnitudes larger than the one on A_r_O2. The comparison between barrier and rate constant clearly indicates that B_r_O2 has a much better reactivity than A_r_O2. Along the catalytic pathway, the reactant is activated by the adsorbed oxygen species on supported Mo catalysts. Therefore the reactivity for A_r_O2 and B_r_O2 is resulted from the different property of the oxygen species. The NBO charge analysis indicate that the oxygen in B_r_O2 has more charges than the counterpart in A_r_O2 which is 0.35 and 0.21 *e* respectively. The more charges localized on the oxygen in B_r_O2 renders a good nucleohphilic ability. On the other hand, it is well documented that the nucleophilic oxygen is more active towards C–H bond activation as the electrophilic oxygen favors the combustion reaction [19,20]. Therefore, the nucleophilic oxygen in B_r_O2 gives a better reactivity.