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Direct conversion of methane to methanol on Fe-Porphyrin: A DFT study

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Abstract

Catalytic oxidation of methane to methanol is one of the most attractive processes for effective natural gas resource utilization. Fe-Porphyrin catalyzed oxidation of methane to methanol with nitrous oxide as an oxidant has been studied by DFT calculation. The nitrous decomposition on the supported Fe particle is the first step with the activation energy of 17.9 kcal/mol. The oxidation of methane to methanol is proposed to be a two-step mechanism: the C-H bond breaking and the methanol formation. The activation energies are 26.6 and 3.0 kcal/mol, respectively. Therefore C-H bond breaking is the rate determining step. Fe-Porphyrin could be a promising material for the oxidation of methane to methanol.

Keywords: Oxidation of methane to methanol, Fe-Porphyrin, DFT, Reaction mechanism

1. Introduction

Methane, derived from natural gas, is the promising source for the renewable energy. Many researchers have been focusing on the conversion of methane to other liquid-phase species in order to increase the efficiency of natural gas utilization. Previously, the two-step process synthesis was used to produce liquid methanol via syngas process with less yield and selectivity. The single-step oxidation reaction of methane to methanol has been recently studied over promising metal-catalysts [1-4].

The supported metal catalysts have been applied to catalyze numerous oxidation reactions. The Fe-Zeolite[1], Cu-Zeolite[2-4] and Fe-Graphene[5] have been used for the oxidation of methane to methanol. Previous studies revealed that Fe metal is a good catalyst for the nitrous oxide decomposition due to its catalytic activity and inexpensive [1, 6]. Beside the high-cost of hydrogen peroxide, nitrous oxide (N_2O) is an important oxidant for the catalytic oxidation reactions [7-8].

Porphyrin is outstanding for its stability and ability to coordinate to almost all of the metal ions [9-10]. Metal-porphyrins have been used as catalyst for several reactions [11-12]. The Fe-Porphyrin catalyst has been used for dimerization of alkenes with $NaBH_4$ under N_2O at ambient condition [13]. The reaction was proposed via the Fe-Porphyrin species while methanol was produced during the reaction. The Density Functional Theory (DFT) has been used to investigate the molecular properties and reaction mechanisms. Over Metal-Porphyrin, several research focus on the methane activation [12] and nitrous oxide decomposition [11]. Previously, we studied the metal-porphyrins for the nitrous oxide composition [14].

In this study, we focus on the oxidation of methane to methanol with nitrous oxide composition. Due to the highly activity for oxidation reaction and the ease of synthesis, we use the Fe-Porphyrin for studying the oxidation reaction. This study will increase the understanding of the reaction mechanism over metal-porphyrin that is crucial for further developing catalysts for methanol conversion industries.
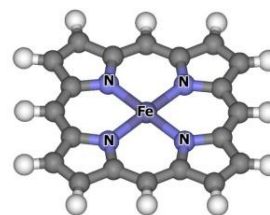

Figure 1 The optimized structure of Fe-Porphyrin with M06-L functional.

2. Methodology

The nitrous oxide decomposition and oxidation of methane to methanol over Fe-Porphyrin was studied with Density Functional Theory, M06-L functional. The Fe-Porphyrin ($FeC_{20}H_{12}N_4$), shown in Figure 1, was used as a model for the catalyst. The mixed basis sets were utilized, i.e. the 6-31G(d,p) level of theory for C, O, N and H atoms and the Stuttgart ECP basis set for Fe atom. The correct spin
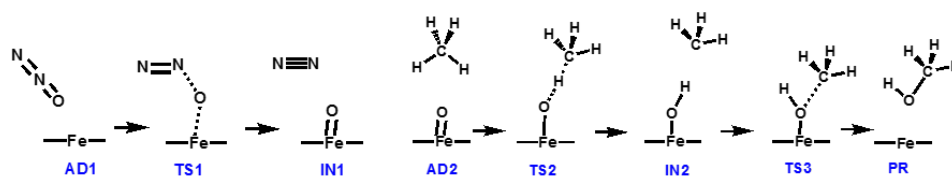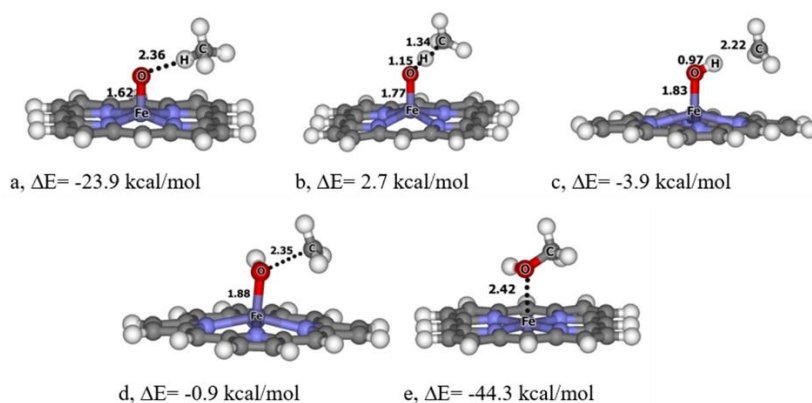
Figure 2 The possible mechanism for the oxidation of methane to methanol with nitrous oxide decomposition over Fe-Porphyrin catalysts.
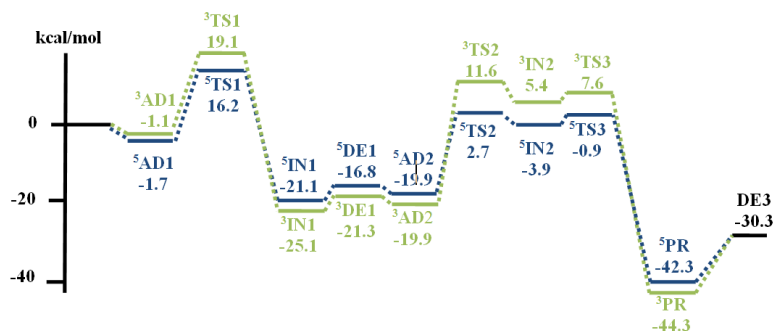
Figure 3 Energy profile of the oxidation of methane to methanol with nitrous oxide decomposition over Fe-Porphyrin catalysts with M06-L functional (Energies are in kcal/mol). The superscript numbers in reaction profiles refer to the stable spin state of each reaction complex.

a, ΔE= -1.7 kcal/mol   b, ΔE= 16.2 kcal/mol   c, ΔE= -21.1 kcal/mol
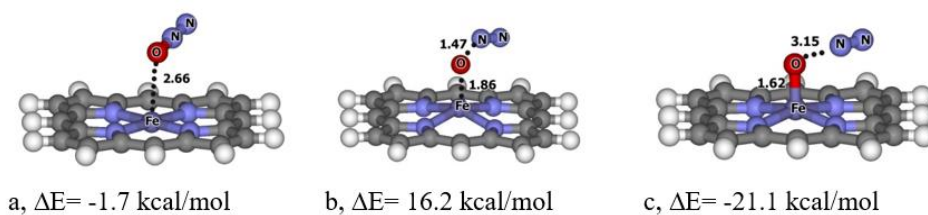
Figure 4 Molecular structure of the nitrous oxide decomposition: (a) ^{5}AD1, (b) ^{5}TS1, (c) ^{3}IN1 on the Fe-porphyrin optimized with M06-L functional. Distances are in Å.

a, ΔE= -23.9 kcal/mol   b, ΔE= 2.7 kcal/mol   c, ΔE= -3.9 kcal/mol

d, ΔE= -0.9 kcal/mol   e, ΔE= -44.3 kcal/mol

Figure 5 Molecular structure of the methane oxidation: (a) ^{3}AD2, (b) ^{5}TS2, (c) ^{5}IN2, (d) ^{5}TS3 and (e) ^{3}PR on the Fe-Porphyrin optimized with M06-L functional. Distances are in Å.

states of all structures were checked by comparing structures with low and high spin states. All calculations were performed by using the Gaussian 09 program.

3. Results and discussion

The reaction mechanism cycle of the nitrous decomposition and oxidation of methane over Fe-Porphyrin is shown in Figure 2. The first half of this reaction was the nitrous decomposition (^{5}AD1, ^{5}TS1 and ^{3}IN1). ^{5}AD1 was the adsorption complex with quintet state. The nitrous oxide decomposition generated an active surface oxygen or α-oxygen on the metal site and released a nitrogen molecule in a single step. The second half was the methane oxidation reaction to methanol. The oxidation was proposed to be two-step mechanism, i.e. the C-H bond breaking of methane (^{3}AD2,^{5}TS2 and ^{5}IN2) and the formation of methanol via the C-O bond forming (^{5}TS3 and ^{3}PR). The relative energies with various spins are shown in Figure 3.

For the first half, the nitrous oxide dissociated on the Fe atom of the Fe-Porphyrin and leaved an oxygen bound to the metal (Figure 4). The nitrous oxide molecule adsorbed on the catalysts by weak interaction between oxygen atom of N_2O and Fe atom ($^5AD1$) with the adsorption energy of -1.7 kcal/mol. At transition state ($^5TS1$), the forming of Fe-O bond over Fe-Porphyrin was responsible for the breaking of O-N bond of N_2O. The activation energy for the catalyzed N-O bond breaking was 17.9 kcal/mol. The intermediate ($^3IN1$) from the first half was N_2 adsorbed on Fe(O)-Porphyrin with the relative energy of -25.4 kcal/mol.

For the second half, all optimized structures of the methane oxidation are shown in Figure 5. Methane weakly adsorbed on the Fe(O)-Porphyrin via H⋯O interaction ($^3AD2$). The reaction was proposed to be a two-step mechanism via methyl radical intermediate ($^5IN2$). In the first step, the C-H bond was broken over the Fe(O)-Porphyrin through the transition state $^5TS2$. The activation energy was 26.6 kcal/mol with the spin crossing. This step was the rate determining step. The methyl radical intermediate then interacted with Fe(OH)-Porphyrin with low activation barrier of 3.0 kcal/mol ($^5TS3$) to form methanol product (^3PR). The methanol molecule was produced with the relative energy of -44.3 kcal/mol and desorbed with desorption energy of 14.0 kcal/mol.

4. Conclusions

The oxidation of methane to methanol with nitrous oxide as an oxidant on Fe-Porphyrin catalysts was studied with M06-L functional. The whole process started with the nitrous oxide decomposition when nitrous oxide adsorbs on Fe-Porphyrin with adsorption energy of -1.7 kcal/mol and decomposed to generate the active surface oxygen with the activation energy of 17.9 kcal/mol. The oxidation of methane to methanol was proposed to be two step of mechanism: the C-H bond breaking of methane and the methanol formation. The C-H bond breaking is rate determining step with activation energy of 26.6 kcal/mol.

5. Acknowledgements

6. References

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