Fusion Engineering and Design 95 (2015) 91–98

Contents lists available at ScienceDirect

Fusion Engineering and Design

journal homepage: www.elsevier.com/locate/fusengdes

Theoretical investigation of the mechanism of tritiated methane dehydrogenation reaction using nickel-based catalysts

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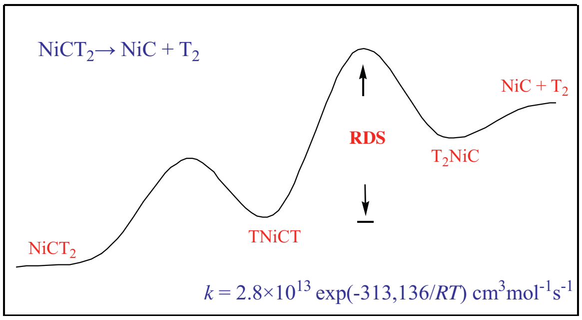
HIGHLIGHTS

- Four-step dehydrogenation of CT_4 catalyzed by Ni to form Ni–C by releasing T_2.
- The process of $Ni + CT_4 \rightarrow NiCT_2 + T_2$ is more achievable than that of $NiCT_2 \rightarrow NiC + T_2$.
- $TNiCT \rightarrow T_2NiC$ step is the RDS with the rate constant of $k = 2.8 \times 10^{13} \exp(-313{,}136/RT)$.
- The hydrogen isotope effect value of k_H/k_T is 2.94, and k_D/k_T is 1.39.
- CH_4 and CD_4 dehydrogenations are likely to occur, accompanied by the CT_4 cracking.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 October 2014
Received in revised form 8 April 2015
Accepted 22 April 2015
Available online 8 May 2015

Keywords:
Density functional theory
Tritiated methane dehydrogenation
Nickel
Reaction mechanism

ABSTRACT

The mechanism of tritiated methane dehydrogenation reaction catalyzed by nickel-based catalyst was investigated in detail by density functional theory (DFT) at the B3LYP/[6-311++G(d, p), SDD] level. The computational results indicated that the dehydrogenation of tritiated methane is endothermic. The decomposition of tritiated methane catalyzed by Ni to form Ni-based carbon (Ni–C) after a four-step dehydrogenation companied with releasing tritium. After the first and second dehydrogenation steps, $Ni + CT_4$ formed $NiCT_2$. After the third and fourth dehydrogenation steps, $NiCT_2$ formed NiC. The first and second steps of dehydrogenation occurred on both the singlet and triplet states, and the lowest energy route is $Ni + CT_4 \rightarrow {}^1COM \rightarrow {}^1TS1 \rightarrow {}^3IM1 \rightarrow {}^3TS2 \rightarrow {}^3IM2$. The third and fourth steps of dehydrogenation occurred on both the singlet and quintet states, and the minimum energy reaction pathway appeared to be $IM3 \rightarrow {}^1TS4 \rightarrow {}^5IM4 \rightarrow {}^5TS5 \rightarrow {}^5IM5 \rightarrow {}^5pro + T_2$. The fourth step of dehydrogenation $TNiCT \rightarrow T_2NiC$ was the rate-determining step of the entire reaction with the rate constant of $k_2 = 2.8 \times 10^{13} \exp(-313{,}136/RT)$ (in $cm^3\ mol^{-1}\ s^{-1}$), and its activation energy barrier was calculated to be 51.8 kcal/mol. The Ni-catalyzed CH_4 and CD_4 cracking dehydrogenation processes are also investigated and the hydrogen isotope effect is evaluated. The hydrogen isotope effect value of k_H/k_T is computed to be 2.94, and the value of k_D/k_T is computed to be 1.39. The catalytic dehydrogenation reactions of methane and deuterated methane are likely to occur, accompanied by the tritiated methane catalytic cracking reaction in the fusion process.

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http://dx.doi.org/10.1016/j.fusengdes.2015.04.051
0920-3796/

1. Introduction

In the fusion process of deuterium and tritium at International Thermonuclear Experimental Reactor (ITER), the interaction of deuterium, tritium, and the first wall material produces a large amount of deuterated and tritiated methane. Methane gas is considered to be a major impurity in plasma exhaust gas. It is very important to recycle the deuterium and tritium in the plasma exhaust gas of ITER. So far, catalytic cracking of methane is the most affordable method to produce hydrogen [1–3]. Thus, the tritiated methane catalytic cracking dehydrogenation reaction is intriguing for fusion waste recycling studies.

Nickel-based catalysts are inexpensive and have high activity; therefore, it is the most common catalyst used in methane catalytic cracking reactions [4–6]. As a classic transition metal, nickel atoms or ions in the gas phase can react with methane as the active species. By simplifying the reaction, we were able to understand the process of selective breaking of aliphatic C—H bonds [7–12]. Thus, the methane dehydrogenation reaction is of great interest in both the experimental field and theoretical calculations. Blomberg et al. [13,14] studied the Ni insertion process on methane C—H bonds by using CASSCF, CCI, and IC-ACPF methods. Burghgraef et al. [15,16] studied the activation of the methane C—H bond catalyzed by a Ni atom by using density functional theory (DFT) method. Wittborn et al. [17] used the PCI-80 (MCPF) method to verify the previously reported calculations, which used the Becke 3 Lee Yang Parr (B3LYP) functional and found that it was highly suitable for studying the $Ni + CH_4$ reaction system. All these studies focused on the insertion of Ni into the methane C—H bond, i.e., $Ni + CH_4 \rightarrow HNiCH_3$ Yang et al. [18] used DFT to study the reaction of $Ni(d^{10}\,{}^1S)$ with the methane C—H bond. They applied the Stuttgart-Dresden (SDD) pseudopotential for the Ni atoms and concluded that the carbene formation step (i.e., $CH_4 \rightarrow (H_2)NiCH_2$) is the rate-determining step (RDS) of the reaction. Subsequently, they applied the B3LYP functional with augmented bases (B3LYP/6-311++G(2d, 2p) and B3LYP/6-311++G(3df, 2p)) and studied this process in detail [19].

Although there are many theoretical studies on Ni-catalyzed CH_4 dehydrogenation, CT_4 dehydrogenation reaction has not been well studied. In addition, the investigations mostly focus on the initial reaction step of removing one atom or molecule of hydrogen from CH_4. The detailed information at molecular level about the mechanism of the subsequent steps is much less known. In order to thoroughly understand the CT_4 dehydrogenation mechanism and clarify the Ni catalysis steps in detail, we have used the DFT to study the Ni-catalyzed CT_4 dehydrogenation reaction, with the aim of completing the theoretical studies about the tritiated methane cracking reaction and providing references for further experiments. Furthermore, we calculate the rate constants of the tritiated methane cracking process. Since the three hydrogen isotopes all present in the nuclear fusion facility, we evaluate the hydrogen isotope effect.

2. Computational method

Among the correlated functional theories, B3LYP performs well for the metal catalyzed reactions [20–23]. The previous investigation also indicated that B3LYP method can give reasonable structures and energies for the $Ni + CH_4$ reaction system [17,18]. All calculations were performed at the DFT level, by means of the hybrid B3LYP [24–26] functional method, as implemented in Gaussian 09 program [27]. Ni atom was described using an effective core potential (SDD) [28] for the inner electrons, and its associated double-ζ basis set for the outer ones. The 6-311++G(d, p) [29,30] basis set was used for the C, T, H and D atoms. Zero-point vibrational energy (ZPVE) corrections were also applied in relative energies in the gas phase. Vibrational frequencies for all optimized structures were also obtained at the B3LYP/[6-311++G(d, p), SDD] level. The intermediates did not have any imaginary frequencies while the transition states had only one imaginary frequency. For every transition state, the intrinsic reaction coordinate (IRC) calculations were performed to further verify that the optimized transition state correctly connects the relevant reactant and product [31,32]. Rate constants were also calculated according to conventional transition state theory (TST) [33], including a tunneling correction based on Winger's formulation [34]. The hydrogen isotope effects were calculated on the basis of transition state theory at $p = 1$ atm and $T = 973.15$ K (700 °C).

3. Results and discussion

3.1. Mechanism

Since nickel atom is the widely accepted catalytically active species for C—H activation of methane, we continue the previous proposal [13–19] considering Ni species as the effective catalytic species in this reaction. Our calculations start from the simulation on the reaction of $Ni + CT_4$. Because the electronic configuration of nickel is $[Ar]3d^84s^2$ ([Ar] represents the electronic configuration of Ar), the reaction between nickel and CT_4 can occur with Ni on either the singlet or the triplet state. When CT_4 loses a molecule of tritium under Ni catalysis and transforms into $NiCT_2$, the reaction can occur on either the singlet or the quintet state. Thus, we separated the reaction into two parts, $Ni + CT_4 \rightarrow NiCT_2 + T_2$ and $NiCT_2 \rightarrow NiC + T_2$, for further investigation.

3.1.1. $Ni + CT_4 \rightarrow NiCT_2 + T_2$

Because of the electronic configuration of Ni, the Ni-catalyzed CT_4 dehydrogenation can occur on both the singlet and triplet states. DFT calculations were used to optimize each structure for the open-shell singlet and triplet states as well as to obtain their relative energies. The total energies *Ec* and relative energies ΔE of the species corrected by ZPVE with respect to reactants in the gas phase at the B3LYP/[6-311++G(d, p), SDD] level for the singlet and triplet states are listed in Table 1. Fig. 1 shows the calculated reaction energy profiles of Ni-catalyzed CT_4 dehydrogenation at the B3LYP/[6-311++G(d, p), SDD] level. The optimized structures of the related species on the energy profiles are also shown in Fig. 1.

The calculation results show that Ni-catalyzed CT_4 dehydrogenation to form $NiCT_2 + T_2$ consists of two dehydrogenation steps involving two hydrogen migration transition states.

Irrespective of whether the singlet or the triplet state is involved, the dehydrogenation of $Ni + CT_4$ consists of two dehydrogenation steps, as shown in Fig. 1. The process is completed through two transition states of tritium migration. Firstly, Ni combines with CT_4 and forms the binary complex COM. It goes through the transition state TS1 in which the T1 atom of CT_4 migrates toward Ni and forms the intermediate IM1 ($TNiCT_3$). Then, another T atom on the carbon migrates to the Ni atom and forms IM2 (T_2NiCT_2) intermediate. Note that we did not obtain any stable Ni-CT_4 binary complex on the triplet state, however, it did not affect our determination of the lowest energy surface. In ^{1}TS1, the vibrational mode is the T1 atom moving from the C atom to the Ni atom with a vibrational frequency of 570 cm^{-1}. In ^{3}TS1, the vibrational mode is the same as that of the ^{1}TS1, with a vibrational frequency of 3094 cm^{-1}. It is emphasized that during the ^{1}IM1 ($TNiCT_3$) → ^{1}IM2 (T_2NiCT_2) dehydrogenation process, there are two possible tritium migration transition states on the singlet, while there is only one tritium migration transition state on the triplet. As shown in Fig. 1, on the singlet, ^{1}TS2 corresponds to the tritium migration of the T2 atom from the C atom