Computational and Theoretical Chemistry 1073 (2015) 94–101

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

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

A comparison of methane activation on catalysts Pt_2 and PtNi

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ARTICLE INFO

Article history:
Received 8 July 2015
Received in revised form 28 August 2015
Accepted 28 August 2015
Available online 7 September 2015

Keywords:
Methane activation
DFT
Bimetallic catalysts
Reaction path

ABSTRACT

The microscopic mechanisms of methane activation on the surface of two catalysts Pt_2 and PtNi are studied, using the B3LYP method of Density Functional Theory (DFT). Two reaction paths of methane activation by platinum dimer Pt_2, path A and path B, were studied in the paper. On the basis of the co-adsorption of CH_x ($x = 0–3$) and H on catalysts Pt_2 and PtNi, the results indicate that the activation of methane induced by catalysts platinum dimer Pt_2 and bimetallic PtNi is an endothermic reaction. For the methane activation on platinum dimer Pt_2, the reaction path B is more thermodynamically favored than path A. The activation of the first C–H bond is easier than the second C–H bond on both catalysts. The formation of CH(s) is the RDS on the catalysts Pt_2 (path B) and PtNi for methane activation. The activity and the anti-carbon deposition of the platinum dimer Pt_2 is higher than the bimetallic catalyst PtNi, while the catalyst Pt_2 is not suitable for large scale application.

1. Introduction

With the rapid development and widely application of MEMS technology, micro-combustors have successfully attracted the attention of many researchers, the micro-combustion related problem has also become a hot issue in recent years [1–6]. As is known to all, micro-combustor has a larger surface area to volume ratio, which could directly lead to more heat loss and more free radicals adsorption on the solid wall, the ignition and stable combustion of the internal mixture gas become more difficult. The catalytic combustion method has been proposed to realize energy conversion in micro-combustors [7,8]. The catalytic layer deposited on the reactor walls could reduce the impact of thermal quenching and sustain the chemical reactions at lower temperatures. Transition metals [9–11] have been widely used as the catalysts due to their good catalytic activity and high temperature resistance, oxidation resistance, corrosion resistance and other excellent comprehensive properties. However, the complexity of the surface catalytic reaction and the limitations of experiment method bring many basic problems which still could not be understood, such as detailed reaction paths, catalytic reaction selectivity and the stability of the intermediate complex. Thus, aiming to find out more suitable catalysts, some scholars [12–16] focused on the reaction mechanisms of hydrocarbons catalytic combustion.

In recent years, quantum chemical calculation, a theoretical research method, has been gradually applied to the field of catalytic combustion [17–21]. Surface structures, chemical reaction pathways, bond energies and optical properties of catalysts have been studied at molecular level. Therefore, many experimental phenomena could be reinterpreted to provide substantive advice and to guide the selection and modification of catalysts. A series of studies have shown that lots of guidance significance results on the transition metal surface have been obtained by adopting quantum chemistry software, such as the adsorption [22–24], oxidation [25–28], reforming [18,19,29] of hydrocarbons as well as the combustion mechanism [26,27]. Burch et al. [30] studied the dissociation of C–H bond of different hydrocarbons on the surface of the metal oxides and metal catalysts, they found that C–H bond cracks through the way of homolysis or heterolysis on the surface of metal oxides. As one of the most stable structures of organic molecules, CH_4 activation is much more difficult than other hydrocarbons. Many research indicated that the dehydrogenation reaction of CH_4 is a critical step of many important chemical reactions [22,27,31], such as methane activation is the first step for methane partial oxidation to generate syngas [32], C–H bond cracking [33] is also the first step for the complete combustion of CH_4. Thus, in order to improve the combustion rate and efficiency, it is very necessary to make clear the process of C–H bond activation in methane catalytic combustion.

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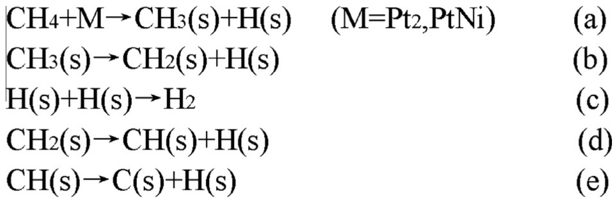
http://dx.doi.org/10.1016/j.comptc.2015.08.016
2210-271X/



$CH_4+M \rightarrow CH_3(s)+H(s)$ (M=Pt2,PtNi) (a)

$CH_3(s) \rightarrow CH_2(s)+H(s)$ (b)

$H(s)+H(s) \rightarrow H_2$ (c)

$CH_2(s) \rightarrow CH(s)+H(s)$ (d)

$CH(s) \rightarrow C(s)+H(s)$ (e)

Fig. 1. Mechanism of methane activation by bimetallic catalyst M (M = Pt_2, PtNi).

Currently, Density Functional Theory (DFT) study of methane activation primarily focused on the transition metal surfaces, such as the 3d metals (where 3d represents Ni, Co, Fe, Mn, Cr, V, and Ti) [34,35], Ni [36], Fe [37], Rh [38], Pt [38–40], Pd [20] and Ru [38]. Liu et al. [41] theoretically studied the mechanism of methane activation on the surface of Rh_n^+ (n = 1–3). Using DFT and slab model, Zhang and Hu [42] studied each step of methane dehydrogenation on the Pd(100) surface. Compared with single metal catalyst, bimetallic catalyst has been widely used in heterogeneous catalytic reaction due to its unique and excellent catalytic properties. Through the comparison of methane catalytic activity on homonuclear bimetallic Ni–Ni, Pt_2^+ and heteronuclear bimetallic NiM^+ (M = Cu, Au, Ag), Yang et al. [36] found that bimetallic nickel (Ni–Ni) is more favored to the thermodynamic properties during methane dehydrogenation reaction. Sun et al. [37] explored the activation of C–H bond in methane by the iron atom, Fe, and the iron dimer Fe_2, they found that the iron dimer Fe_2 has a stronger catalytic effect on the activation of methane than the iron atom.

The study of platinum has been mainly focused on the models of clusters, crystal surfaces, ions, oxides, etc. Liu et al. [40,43] investigated the methane activation by catalyst $[Pt(H)(OH)]^+$, and indicated $[Pt(H)(OH)]^+$ is less reactive than Pt^+ on the activation of methane. So far, the reports on the comparative of methane activation about catalysts Pt_2 and PtNi are relatively few, the thermodynamic parameters and the rate-determining step (RDS) for methane activation can provide useful information for the realistic and complicated catalytic systems. In order to find out the RDS of methane activation by platinum dimer Pt_2 and bimetallic PtNi, DFT calculations have been performed in this work. The activation energy and reaction rate constants along the reaction path are also compared, this comparison is very helpful to understand the methane activation mechanism.

2. Calculation methods

Electron correlation effects are taken into consideration when using DFT [38,40,44]. B3LYP [38–40] method combined with Genecp basis set, where LANL2DZ [38,45] basis set is used for metal atoms Pt and Ni and 6-311G+(d) [38] basis set is used for C and H atoms, have been employed in the structural optimization for all reactants, products, intermediates and transition states (TSs) involved in the reactions of methane activation. The metal atoms Pt and Ni are relaxed during geometrical optimizations. The selected method has been widely applied to structure calculations on systems containing transition metals, and has been proven to combine reasonable computational cost with sufficient accuracy for transition metal systems [36,40].

The vibrational frequencies of all stationary points have been calculated and the zero point energy (ZPE) corrections have been performed at the same theory level. Transition state (TS) has only one imaginary vibration frequency, all of the reactants, intermediates and products have no imaginary frequencies. Furthermore, intrinsic reaction coordinate (IRC) calculations have been carried out to verify that the optimized transition states correctly connect the relevant reactants and products. All calculations were performed with the Gaussian09W program package [46].

In the paper, the energy barrier (E_b) is presented by the difference of Gibbs free energy between transition state and initial state. The reaction energy (Er) is given by the difference of enthalpy between final state and initial state.

$$E_b = \Delta G^{\neq} = G^{TS} - G^{IS} \tag{1-1}$$

$$Er = H^{FS} - H^{IS} \tag{1-2}$$

where G^{TS} is the Gibbs free energy of transition state, G^{IS} is the Gibbs free energy of initial state. H^{FS}, H^{IS} is the enthalpy of final state and initial state, separately.

According to the thermodynamics process of transition state theory (TST), the Arrhenius activation energy (Ea) is given by:

$$\begin{aligned} Ea &= RT + \Delta U^{\neq} \\ &= RT + \Delta H^{\neq} - \Delta n^{\neq} RT \\ &= \Delta H^{\neq} + (1 - \Delta n^{\neq}) RT \\ &= \Delta H^{\neq} + nRT \end{aligned} \tag{1-3}$$

where R is the gas constant, T is reaction temperature, $\Delta U^{\neq}$, $\Delta H^{\neq}$ denotes the change of internal energy, enthalpy between transition state and initial state, respectively. n is the number of molecules involved in the reaction.

When $n = 1$, activation energy Ea is given as follows under constant pressure:

$$Ea = RT + \Delta H^{\neq} \tag{1-4}$$

During the DFT study of methane activation, the temperature and pressure were settled as constants in the Gaussian09W software package. So the pre-exponential factor A and rate constant of a reaction k can also be determined according to TST [47,48]:

$$\begin{aligned} A &= \frac{k_B T}{h} e^n \exp\left(\frac{\Delta S^{\neq}}{R}\right) \\ &= \frac{k_B T}{h} e \cdot \exp\left(\frac{\Delta S^{\neq}}{R}\right) (n = 1) \end{aligned} \tag{1-5}$$

where $\Delta S^{\neq}$ is the entropy difference between transition state and initial state, k_B is the Boltzmann constant and h is the Planck constant.

Define that:

$$\begin{aligned} \Delta G^{\neq} &= -RT \ln K^{\neq} \\ &= \Delta H^{\neq} - T\Delta S^{\neq} \end{aligned} \tag{1-6}$$

The reaction rate constant k can be gotten as following:

$$\begin{aligned} k &= \frac{k_B T}{h} K^{\neq} \\ &= \frac{k_B T}{h} \cdot \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) \\ &= \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \end{aligned} \tag{1-7}$$

where $K^{\neq}$ is thermodynamic equilibrium constant. Eq. (1–7) is the rate constant formula of transition state theory.

3. Reaction mechanisms

Many studies have demonstrated that methane dehydrogenation is completed gradually by four steps [36–38,43,49]. In order to find out the catalytic effect on methane, the mechanism of methane activation by catalysts Pt_2 and PtNi was studied with