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Theoretical study on the reaction mechanism of CH_4 with CaO

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Abstract

The reaction pathways and energetics for the reaction of methane with CaO are discussed on the singlet spin state potential energy surface at the B3LYP/6-311+G(2df,2p) and QCISD/6-311++G(3df,3pd)//B3LYP/6-311+G(2df,2p) levels of theory. The reaction of methane with CaO is proposed to proceed in the following reaction pathways: $CaO + CH_4 \rightarrow CaOCH_4 \rightarrow [TS] \rightarrow CaOH + CH_3$, $CaO + CH_4 \rightarrow OCaCH_4 \rightarrow [TS] \rightarrow HOCaCH_3 \rightarrow CaOH + CH_3$ or $[TS] \rightarrow CaCH_3OH \rightarrow Ca + CH_3OH$, and $OCaCH_4 \rightarrow [TS] \rightarrow HCaOCH_3 \rightarrow CaOCH_3 + H$ or $[TS] \rightarrow CaCH_3OH \rightarrow Ca + CH_3OH$. The gas-phase methane–methanol conversion by CaO is suggested to proceed via two kinds of important reaction intermediates, $HOCaCH_3$ and $HCaOCH_3$, and the reaction pathway via the hydroxy intermediate ($HOCaCH_3$) is energetically more favorable than the other one via the methoxy intermediate ($HCaOCH_3$). The hydroxy intermediate $HOCaCH_3$ is predicted to be the energetically most preferred configuration in the reaction of $CaO + CH_4$. Meanwhile, these three product channels ($CaOH + CH_3$, $CaOCH_3 + H$ and $Ca + CH_3OH$) are expected to compete with each other, and the formation of methyl radical is the most preferable pathway energetically. On the other hand, the intermediates $HCaOCH_3$ and $HOCaCH_3$ are predicted to be the energetically preferred configuration in the reaction of $Ca + CH_3OH$, which is precisely the reverse reaction of methane hydroxylation.

Keywords: CaO; CH_4; CH_3OH; Ca; B3LYP

1. Introduction

Recently, the activation of methane has attracted significant attention because of its scientific and industrial importance [1]. Its conversion into more easily handled and stored products, in particular, such as methanol or ethylene, has been extensively studied [1–6]. Theoretical approach starting from the gas phase reactions has been considered to be informative to understand the reaction mechanisms for the more complicated processes of heterogeneous or enzymatic methane monooxygenase catalysis [1].

The activation of C–H bond in methane by various metal oxide ions in the gas phase has been investigated experimentally and theoretically by a number of groups [7–16]. Schwarz's group has systematically examined the efficiency and product branching ratio of the gas phase reactions of various transition metal oxide ions with methane. It is found that transition metal oxide ions, ScO^+, TiO^+, VO^+, and CoO^+, do not react, while the other transition metal oxide ions, MnO^+, FeO^+, NiO^+, PtO^+, and OsO^+, react with methane [9,10]. Additionally, Schwarz, Armentrout and Yoshizawa et al. have comprehensively studied the potential energy surfaces for methane activation by first-row transition metal oxide ions (MO^+s), where M is Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, and suggested that the methane-to-methanol conversion can occur by the following mechanism: $MO^+ + CH_4 \rightarrow OM^+(CH_4) \rightarrow TS1 \rightarrow HO\text{–}M^+\text{–}CH_3 \rightarrow TS2 \rightarrow M^+(CH_3OH) \rightarrow M^+ + CH_3OH$,

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where M is a transition metal, and the inserted hydroxy intermediate, $HO–MO^+–CH_3$, plays an important role in this gas-phase reaction [7,8,11–16]. These authors concluded that the experimentally observed reaction efficiency and methanol/methyl product branching ratio can be rationalized in terms of the calculated barrier heights at TS1 and TS2.

The reaction mechanism of methane with neutral metal oxides in the gas phase has also been theoretically investigated by several groups [17–23]. Børve et al. have performed ab initio calculations on the direct abstraction of a hydrogen atom from methane via M–O–H–C collinear geometrical transition state using gas-phase LiO, MgO, and AlO, respectively [17]. Broclawik et al. have used density functional calculations to study the activation of methane over MO (M = Pd, Rh), and found that MO can insert into the C–H bond of CH_4 and lead to the formation of the hydroxy intermediate ($HOMCH_3$) [18,19]. Recently, Hwang et al. have theoretically studied the reaction mechanism of MO (M = Be, Sc, Ni, Pd, Pt) with methane, and comparatively analyzed the possibility of the formation of $M + CH_3OH$ and $MOH + CH_3$ [20–22]. Previously, we have reported the reaction mechanism of MgO and CH_4, and proposed that the formation of $MgOH + CH_3$ proceeds more easily than the other one of $Mg + CH_3OH$, and the hydroxy intermediate $HOMgCH_3$ is energetically preferred [23]. CaO has been experimentally found to be one of the most effective catalysts in the oxidative coupling of methane, where CH_4 and O_2 are converted to C_2 hydrocarbons (C_2H_4 and C_2H_6) [2–6]. However, neither mechanistic nor quantum-chemical studies have yet been conducted for the very interesting gas-phase processes. The goal of the present paper is to study the potential energy diagram from $CaO + CH_4$ to $Ca + CH_3OH$ and $CaOH + CH_3$ and to provide reliable structures of the reactants, intermediates, transition states, and products as well as their chemically accurate energetics.

2. Computational details

Computations were carried out with the Gaussian 03 program [24]. Full geometry optimizations were run to locate all of the stationary points and transition states on the singlet spin state potential energy surface (PES) for the reaction of $CaO + CH_4$ at the B3LYP/6-311+G(2df,2p) level of theory. The stability of the density functional theory (DFT) wavefunction was tested. If an instability is found, the wavefunction is reoptimized with the appropriate reduction in constraints, and the stability tests and reoptimizations are repeated until a stable wavefunction is found. The spin-unrestricted version of the B3LYP (UB3LYP) method was applied even to singlet states when the reaction species are reasonably considered to have an open-shell-singlet electronic configuration. Computed $\langle S^2 \rangle$ values suggested that no spin contamination is included in the calculations, except in open-shell-singlet calculations. Systematic frequency calculations were performed to characterize stationary points obtained and to take corrections of zero-point vibrational energy (ZPE) into account. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding minima [25,26]. Concerning the basis set superposition errors (BSSE), counterpoise corrections were used on an energy calculation, geometric optimization, and frequency calculation for molecular intermediates $CaOCH_4$ and $OCaCH_4$ [27,28]. The relative energies of various species were then refined by single-point calculations at the B3LYP/6-311+G(2df,2p) optimized geometries using the QCISD method with the large 6-311++G(3df,3pd) basis set, QCISD/6-311++G(3df,3pd)//B3LYP/6-311+G(2df,2p). Unless otherwise mentioned, all relative energies is with respect to reactants [$CaO(^1\Sigma) + CH_4$] at the QCISD/6-311++G(3df,3pd)//B3LYP/6-311+G(2df,2p) level of theory, including ZPE corrections obtained at the B3LYP/6-311+G(2df,2p) level.

3. Results and discussion

Zero-point energies (ZPE), total energies corrected by ZPE, and relative energies of various compounds in the reaction of CH_4 with CaO calculated at the B3LYP/6-311+G(2df,2p) and QCISD/6-311++G(3df,3pd) levels of theory are listed in Table 1, while Table S1 of Supplementary data presents vibrational frequencies for various species. The schematic energy diagram along the $CaO + CH_4$ reaction pathways in the singlet state computed at the QCISD/6-311++G(3df,3pd)//B3LYP/6-311+G(2df,2p) level is shown in Fig. 1. The optimized geometric structures of various reactants, intermediates, transition states, and products are collected in Fig. 2, while Table S2 of Supplementary data lists standard orientation of various compounds calculated at the B3LYP/6-311+G(2df,2p) level.

3.1. Interaction between CaO and CH_4

For the $^1\Sigma$ ground state of CaO, the computed Ca–O distance is 1.809 Å, in agreement with the experimental value of 1.822 Å [29]. The computed dissociation energy (D_0) is 360.5 kJ mol^{-1}, close to the experimental value of 383.0 kJ mol^{-1} [29]. The computed overall energies for the $CaO + CH_4 \rightarrow Ca + CH_3OH$ reaction is endothermic by 11.5 kJ mol^{-1}, as shown in Table 1, in reasonable accordance with the experimental estimation (7.7 kJ mol^{-1}) [29]. These results indicate that the present theoretical method of QCISD/6-311++G(3df,3pd)//B3LYP/6-311+G(2df,2p) is appropriate for the $CaO + CH_4$ system.

Concerning the initial interaction between CaO and CH_4 (Figs. 1 and 2), two models are considered: (i) a side-on to side-on approach of the C–H bond to Ca–O forming $OCaCH_4$ molecular complex with C_1 symmetry, and (ii) a collinear C–H approach to the O-end of the