



Theoretical study of CH₄ adsorption and dissociation on W-Cu(1 0 0) surface

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ABSTRACT

First principle density functional theory calculations (DFT GGA-PW91) have been employed to study the activity of W-doped Cu(1 0 0) surface for methane dissociation. We studied methane site preference for CH₄, CH₃, CH₂, CH, C and H species at a coverage of a 0.25 monolayer. From the calculated adsorption energies, we found that W-doping stabilizes better all species. The top tungsten site is the most stable for methane, methyl and hydrogen. However, the methyn and carbon atoms prefer the fourfold hollow site, while methylene prefer bridge site. In addition, the electronic structure analysis of methane and surface showed a weak chemical interaction. Furthermore, methane complete dehydrogenation mechanism have been investigated in terms of the thermodynamics and kinetics. The results revealed that the W-Cu(1 0 0) is more reactive surface for methane dissociation, thermodynamically and kinetically, rather than others Cu-based catalysts.

1. Introduction

The methane interaction with metal surfaces has a very popular objective of research groups over the last decade due to their industrial applications and complexing properties in particular towards experimentally probe effects of mode specificity [1–3], steric effects [4–5] and bond selectivity [6–7]. Also, this polyatomic molecule can be tractable by a very high theoretical level calculation although its small size [1]. Moreover, the methane proves to be an excellent source of energy around the world and its dissociation is the key feature to produce useful compounds such as hydrogen. However, the decomposition of methane at room temperature is very hard due to the high stability of C–H bond (432 kJ) especially in the gas phase [8]. Therefore, a catalyst is needed to ensure the dissociation process. For that reason, catalytic CH₄ dissociation using transition metals (TM) became an interesting subject and it has been widely studied on different mono and bi-metallic catalyst surfaces [9–13], such as, NiM(1 1 1) [14] where M = Co, Rh, Ir and NiM [15] surfaces with M = Cu, Ru, Rh, Pd, Ag, Pt, Au. In the same way, many other studies on Pd-based surfaces [9,16–21], on Cu-based catalysts [22] and on Rh-based (1 1 1), (1 1 0) and (1 0 0) surfaces [23] have been devoted to elucidate the methane activation mechanism.

The adsorption and dehydrogenation of methane on different metal surfaces have been thoroughly investigated using various experimental techniques [12,24–27] and theoretical methods [11–13,28–36].

Calculation results of the CH₄-surface interaction have enhanced solving the long-standing problems and questions related to interpretation and investigation of experimental measurements. Recently, theoretical studies have proved that the activation energies for methane dissociation on Ni surface were lower than those on Cu surface, which is similar to experimental observations [36–40]. The surface distortions of Cu (1 1 1) and Ni(1 1 1) were scrutinized in order to improve the methane decomposition rate [36,29–30,41]. Moiraghi et al. [42] also used DFT calculations to reinvestigate the dissociative adsorption of methane on Ir(1 1 1) at high temperatures. Their results showed that the distortions of ideal Ir(1 1 1) terraces are more likely to be responsible for the low activation energy pathway observed in experiments at high-surface-temperature and low impact energy molecules. Furthermore, surface distortions are strongly reached when surface temperature decreased. González and al. [43] investigated the methane adsorption on pristine (1 1 1), (1 1 0), and (1 0 0) nickel surfaces, and on stepped Ni(5 3 3) and Ni(5 7 7) surfaces, using Perdew–Burke–Ernzerhof (PBE) function including dispersion terms. They concluded that the interaction is always weak and could be safely classified as a physisorption. Whereas, He et al. [44] focused their attention to the tensile strain influence on CH₄ dissociation on Cu(1 0 0) surface. They found that the strain hinders of methane dissociation process and the CH₄ dissociation rate depends sensitively on the magnitude of the surface tensile strain. However, the advancement of new heterogeneous catalysts for the dissociation of CH₄ is a great challenge for the petrochemical industry. Recently, Carey

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