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Hydrogen abstraction from methane on cristobalite supported W and Mn oxo complexes: A DFT study

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ABSTRACT

The oxidative coupling of methane using the $MnNaW/SiO_2$ catalyst was considered for the W-Mn two-metal-site model on the (111) surface of α-cristobalite by DFT means in the cluster approximation. The crucial step of this process, namely, the hydrogen abstraction from methane is assumed to proceed on whether the terminal W═O or the Mn═O group. The energy barrier for the methane dissociation on the tungsten species was predicted to be much higher than that for manganese. This allows one to suggest that the Mn species are responsible for hydrogen abstraction from methane. The W species are suggested to play a role in the ethane formation on the surface from tungsten bound methoxy group and govern selective oxidative dehydrogenation of ethane.

1. Introduction

Methane is considered as alternative to crude oil for the production of basic petrochemicals [1–3]. Various direct and indirect (through the synthesis gas formation) routes of methane conversion to valuable products have been developed [1–8]. The oxidative coupling of methane (OCM) is an attractive process for direct production of ethane and ethylene from methane. Since the first publication on OCM [9], numerous works have been devoted to this reaction. The $MnNaW/SiO_2$ system is one of the most suitable OCM catalysts that shows both high product yield and long-term stability [10–16]. There is a few contradicting hypotheses concerning the nature of active species in the $MnNaW/SiO_2$ catalyst for the OCM reaction. The surface cluster O═W(—O—Si)$_3$ species with one W═O and three W—O—Si bonds was one of the first models of the active site suggested for this reaction [17]. The DFT study of $MnNaW/SiO_2$ suggested the possibility for the tetrahedral WO_4 species unlike the MnO_4 species to be active sites for methane activation [18]. Contrary to above-mentioned works by Li group, the Na—O—Mn sites were considered as the most possible active centers, on base of the catalytic behaviors of $Mn/Na_2WO_4/MgO$ and $NaMnO_4/MgO$ catalysts [19]. The Mn_2O_3 species were proposed to act as the active sites responsible for the methane activation, while Na^+ and oxo anion (WO_4^{2-}, MoO_4^{2-}, SO_4^{2-}, PO_4^{3-} or $P_2O_7^{4-}$) were thought to affect the formation of specified Mn species [20]. Alternatively, the two-metal site model of active centers was considered by Li and co-workers on the basis of XANES, EXAFS, TPR, TPO and high temperature quenching EPR characterizations [21,22]. According to this model, methane activation takes place on the W^{6+} sites, while activation of gas-phase oxygen occurs on the Mn^{3+} sites. The oxygen spillover from Mn_2O_3 to Na_2WO_4 on surface provides the higher activity of $MnNaW/SiO_2$ catalyst in comparison with that of NaW/SiO_2. Similar results were obtained by Kou et al. using the L-edge and the K-edge XAFS and XPS [23]. It was indicated that the combination of tetrahedral (WO_4) and octahedral (MnO_6) metallic cores with oxidation states being different from each other is responsible for the catalysis in the oxidative coupling of methane. Ji et al. pointed out that both Na—O—Mn and Na—O—W moieties act as the active centers of the catalysts for OCM [12]. These authors noted that tetrahedral WO_4 species is more active and selective for the OCM reaction while the near-surface Mn concentration correlates with the CH_4 conversion and C_2H_4 selectivity. There are different assumptions on the role of the alkali component [12,13,16,24]. In particular, it was demonstrated that Na induces the low-temperature phase transition of amorphous silica support to α-cristobalite and acts to disperse and stabilize the W surface species [13]. The Na presence was assumed to be necessary for the formation of distorted WO_4 species which are responsible for the catalyst activity [24]. In addition, it was found that the presence of Na in the catalyst facilitates the Mn and W migration to the catalyst surface [12].

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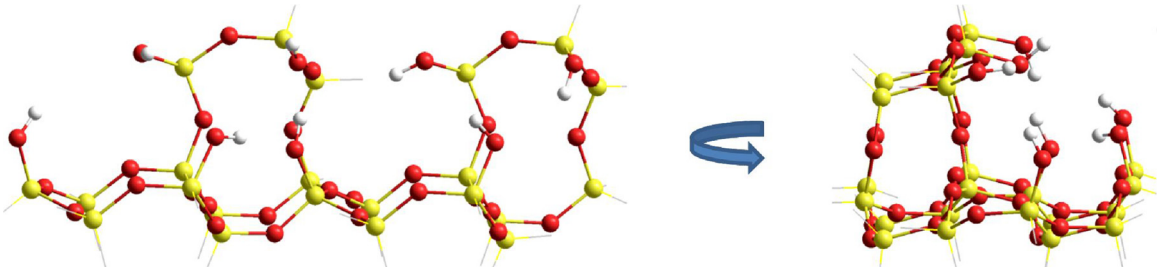

Fig. 1. A cluster model of α-cristobalite with hydroxylated surface (8 OH-groups) used for subsequent calculations (left – front view, right – side view, colour scheme: H – white, O – red, Si – yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Relatively few theoretical investigations have been conducted to determine the structure of the W-Mn active centers in $MnNaW/SiO_2$ catalysts and mechanism of methane dissociation over possible metal sites. Previous studies have focused on the modeling of active center structures on the (111) surface of α-cristobalite using molecular mechanics and DFT [18]. The W oxo species were shown to interact with the silica surface by one or three bridge oxygen atoms to form tetrahedron [WO_4], while Mn interacts with single bridge oxygen to form either dispersed MnO_4 or oxide clusters. As far as other OCM heterogeneous catalysts are concerned, the majority of theoretical studies is devoted to the Li-doped MgO catalyst [25–27]. The activation energy of hydrogen abstraction from methane over such model was estimated to be about 72 kJ/mol [25].

The H abstraction from methane is usually considered as a crucial step in the heterogeneous oxygenation of methane [28,29]. The hydrogen abstraction from the methane molecule has been assumed to be also responsible for the initial methane activation under OCM reaction conditions at 800–900 °C. In this case, a heterogeneous catalyst (Cat) for the O_2 oxidation of methane abstracts a hydrogen atom from methane to release gas-phase methyl radicals, which recombine to form ethane. The latter molecule transforms to ethane after subsequent dehydrogenation in gas phase.

On base of available experimental and theoretical data, one may suggest that the terminal oxo center on whether tungsten or manganese species abstracts hydrogen from methane to form methyl radical, which then readily leaves the surface for the gas phase to participate in the C_2 coupling reactions. It remains unclear which metal (W or Mn) is actually responsible for the hydrogen abstraction. To answer this question the present study performs DFT modeling of the active centers of the $MnNaW/SiO_2$ catalyst using the W-Mn two-metal-site model on the (111) surface of α-cristobalite.

2. Computational details and surface model

All calculations have been performed at the B3LYP level using the LANL2TZ(F) and 6-311G** basis sets for tungsten and manganese and lighter atoms, respectively.

The activation energy (E_a) is estimated by the energy barrier ($\Delta E^{\ddagger}$). We are aware that the activation energy should be Gibbs energy of activation ($\Delta G^{\ddagger}$). However, estimations of $\Delta E^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ for the HAT reaction on oxo-metal centers within DFT showed that these values are usually equal to each other within few kcal/mol (see for example the H abstraction from methane on ferryl moiety in zeolite [30] and on the $Li^+O^{\bullet}$-site of Li-doped MgO [31]). Since we need only a qualitative comparison of the activation energies for the reaction on the W and Mn species which differ by tens of kcal/mol, skipping relatively small zero-point energy and entropy terms seems to be fairly good approximation.

The models for active sites for the $MnNaW/SiO_2$ catalyst have been considered assuming α-cristobalite form of the SiO_2 oxide because according to numerous published data, α-cristobalite is the main phase of SiO_2 support in the composition of as-prepared $MnNaW/SiO_2$ catalysts [11,12,17,32]. This phase remains a key phase under reaction conditions [16].

The (111) surface of α-cristobalite is modeled by a large cluster in which the terminal oxygen atom dangling bonds (Si—O—) are saturated by hydrogen atoms H* (at optimized O—H* distances). In further calculations the H* coordinates are frozen. Hydroxyl groups (≡Si—OH) substitute surface oxygen atoms to which the reaction center is to be attached. Chosen fragment of the (111) surface contains 8 such hydroxyl groups which are conveniently substituted by 2 reaction centers. An optimized cluster model of α-cristobalite is given in Fig. 1.

3. The W-Mn model

For modeling of mononuclear W^{6+}-containing center on the silica surface the $WO(OH)_4$ complex was attached to the above described silica cluster. These centers are built from calculated geometry for the $O{=}W(OH)_4$ molecule which is most stable among various tungsten hydroxides as follows from the benchmark quantum chemical data [33]. Being grafted on the α-cristobalite support via three auxiliary terminal hydroxide groups this hydroxo tungsten complex becomes $O{=}W(OH)(-O-Si)_3$ center coupled to the surface by three Si-O-W bonds after removing three water molecules. Sampling different grafting positions for the $O{=}W(OH)(-O-Si)_3$ species on the surface by changing the number of bonds to the α-cristobalite surface results only in a small energy increase of about 4 kcal/mol when going from three to two Si—O—W bonds.

Above-mentioned strong synergetic effect for the $MnNaW/SiO_2$ catalyst implies that the active center contains neighboring oxo W and Mn species formed from Na_2WO_4 and Mn_2O_3, as was previously proposed by Li [21]. To model such binuclear center, the oxo complex of Mn^{3+} was designed on the surface in the neighborhood of the $O{=}W(OH)(-O-Si)_3$ species (Fig. 2). In this site, the tungsten and manganese atoms are indirectly coupled via the two Si—O—Si bonds of the support. The active sites of this model does not contain in fact silanol groups. This assumption is based on the experimental observation that the number of the hydroxyl groups on the surface of silica is only 5.0 per nm^2 for a fully hydroxylated surface independently of the silica type. At the OCM reaction temperatures (>1000 K) the silanol number drops to 1.0 per nm^2 [34].

The Na component of the $Mn/Na_2WO_4/SiO_2$ catalyst was not considered in the model because it is responsible mostly for the formation of catalyst support structure, converting amorphous silica (which burns methane and hydrocarbon product) into α-cristobalite (which is inert under reaction conditions) as was shown by experimental means in the work by Lambert and coworkers [13]. We proceed with the model describing the catalyst having α-cristobalite support.

The Mn^{3+} center in the two-metal model possesses four d electrons that makes non-zero spin states energetically most favorable taking into account the weak oxo ligand field. Therefore, it is not