



Research paper

# Insight into mechanism of iron-oxides reduction in atmospheres of CH<sub>4</sub> and CO

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## ARTICLE INFO

## Article history:

Received 11 May 2018

In final form 12 July 2018

## Keywords:

Iron oxide

Carburization

CO conversion

CH<sub>4</sub> conversion

DFT

IRC

NBO

## ABSTRACT

First-principle calculations are carried out to interpret the experimental observations and to generate the mechanisms of CO and CH<sub>4</sub> conversion with Fe<sub>2</sub>O<sub>1-3</sub>. The stabilization of Fe–C bonding involves π\*(C–O) and electron donating from oxygens' LP. The Fe–O bond activation is rate-limiting step of conversions. Stabilization and activation are affected by number of oxygens at the iron active site. Low ORBs are identified for CO + Fe<sub>2</sub>O<sub>1-3</sub> reaction pathways. Significant ORBs are calculated for Fe<sub>2</sub>O<sub>3</sub> + CH<sub>4</sub>, and the competing mechanism of reduction by H<sub>2</sub> is shown. DFT calculations suggest favorable formation of Fe<sub>3</sub>C in atmosphere of CH<sub>4</sub> and its oxidation in atmosphere of CO.

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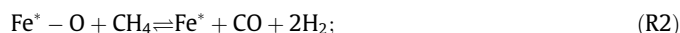
## 1. Introduction

Oxy-iron compounds (OIC) are known to be an important group of industrial heterogeneous catalysts [1]. The reactivity of OIC clusters toward various gas-phase molecules has been extensively investigated experimentally with emphasis on rate limiting steps in practical catalytic cycles. More can be found in Schroder et al. [2] review. However, molecular-level mechanisms of some processes catalyzed by OICs and the possible side-reactions are unclear. Recently, Ca–Fe based catalysts attracted an interest due to their potential in chemical looping hydrogen generation (CLHG) process [3,4]. Sun et al. [3] have shown that higher yields of hydrogen could be generated by using a novel Ca–Fe based oxygen carriers, which is proved to be a more stable formation of the calcium ferrite compounds and promising catalysts for CLHG process which show perfect reducibility, oxidation activity, and cyclic stability. Several types of compounds are known to participate in the Ca–Fe based catalysts [5]. In the Fe<sup>3+</sup>-containing system of CaO–Fe<sub>2</sub>O<sub>3</sub>, the calcium ferrites with different molecular ratios are known: 2CaO–Fe<sub>2</sub>O<sub>3</sub>, CaO–Fe<sub>2</sub>O<sub>3</sub> and CaO–2Fe<sub>2</sub>O<sub>3</sub>. The Fe<sup>n+</sup>-containing systems of CaO–Fe<sub>x</sub>O<sub>y</sub> usually exhibiting a layered structure containing 3d<sup>6</sup> iron atom in a high- and low spin distorted squareplanar

coordination. This structure complicates the modeling and theoretical study of their catalytic activity and side-effects. For instance, the 2:1 compound, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, which is considered as an oxygen-deficient perovskite of the Brownmillerite-type of structure, exhibits the alternating tetrahedral and octahedral layers [5]. However, in spite of specific role of the incorporated alkaline earth metals (Mg, Ca, Be, Sr, Ba, Ra) in the ferrites catalysts, the basic concept is that a catalytic reaction occurs at specific catalytically active sites of iron [6,7]. That is why, we suppose that small gas-phase iron oxide clusters (neutral) composed of limited numbers of iron atoms could serve a good model system to investigate the intrinsic reaction mechanisms in OIC.

In this study we investigate the reactivity of iron oxide clusters (Fe<sub>x</sub>O<sub>y</sub>) toward CH<sub>4</sub> and CO and the possible carburization of iron active sites. The iron active site (Fe\*) is reduced and regenerated by the following general reactions:

(a) CO conversion:

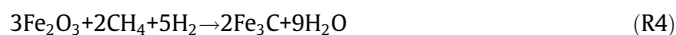
(b) CH<sub>4</sub> conversion:

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The mentioned above reduction experiments [3] revealed that oxygen carriers oxidize significantly smaller amount of  $\text{CH}_4$  species compared to CO. Additionally, a weight increase has been observed from both CO and  $\text{CH}_4$  conversions when the oxygen carrier was about to be completely reduced or was completely reduced. Frequently, in processes where gas mixtures containing CO or hydrocarbons, (such as methane and other gases) contact with the OIC at high temperature the problems with carburization can occur. According to the general reactions of carburization (R3, R4), the  $\text{Fe}_3\text{C}$  should form in presence of both, CO and  $\text{CH}_4$ . Meanwhile, in Fan et al. [3] experiments XRD analysis of final products revealed that all the CO reduced Ca–Fe based oxygen carriers existed in the form of CaO and Fe and none of the  $\text{Fe}_3\text{C}$ . At the same time, in atmosphere of methane,  $\text{Fe}_3\text{C}$  began to gradually accumulate. The possible reactions of carburization with different reducing agents are the following:



In spite of importance of developing of sufficient technologies of CO and  $\text{CH}_4$  oxidation, there exists a certain lack of comprehensive and systematic studies of the intrinsic reaction mechanism. This includes details how CO and  $\text{CH}_4$  oxidation are catalyzed at a molecular level and what is a nature of side reactions. Various proposed mechanism arises according this issue. Li et al. concluded that the small particle size and the FeOOH component of their  $\text{Fe}_2\text{O}_3$  catalyst contribute to the high catalytic performance [8]. Zheng et al. concluded that the high density of Fe atoms on the exposed {1 1 0} planes of their quasicubic R- $\text{Fe}_2\text{O}_3$  nanoparticles leads to the excellent catalytic reactivity [9]. Xue et al. observed significant reaction barriers for the reactions of  $\text{Fe}_2\text{O}_{4-5}$  with CO. The rate-limiting steps for this processes involve the O–O activation [10]. Huang et al. [11] explored processes of methane dissociation, on a- $\text{Fe}_2\text{O}_3$  (0 0 1) surface and found that sequential dissociations of  $\text{CH}_4$  have the highest barriers. The formed H atoms may recombine to produce  $\text{H}_2$  with significant activation barrier of at least 1.37 eV. In addition, they concluded that the CO production is more favorable than  $\text{CO}_2$ . First principle calculations were also used by Reddy and co-workers to study CO oxidation catalyzed by a neutral  $\text{Fe}_2\text{O}_3$  cluster [12]. CO adsorption onto gas-phase  $\text{Fe}_2\text{O}_3$  clusters causes rearrangement of one of the three Fe–O–Fe bridged bonds to one Fe–O terminal bond. A reaction barrier of 0.39 eV was calculated for CO approaching the  $\text{Fe}_2\text{O}_3$  cluster. The Fe–O terminal bond can further oxidize another CO molecule to form  $\text{CO}_2$  easily. The gas-phase experimental study by Xue et al. [10] for the neutral clusters later support those theoretical results.

In current study, the first-principle calculations (DFT) are used to explain the reactivity of OIC toward CO and  $\text{CH}_4$  and to elucidate the results of experimental studies of Fan and co-workers [3,13]. The  $\text{Fe}_x\text{O}_y$  clusters have been used as the model of active sites. The details of the reaction mechanism are obtained and used to interpret at a molecular level catalytic process of CO and  $\text{CH}_4$  oxidation by oxygen of OIC and the side-reaction mechanism of  $\text{Fe}_3\text{C}$  formation. The lattice oxygen of oxygen carrier, which involves in the real CLHG reactions is not under consideration in current study.

## 2. Computational methods

The quantum chemical calculations using the Gaussian 09 program [14] have been employed to study the multicycles of CO and  $\text{CH}_4$  reduction on the  $\text{Fe}_2\text{O}$ ,  $\text{Fe}_2\text{O}_2$  and  $\text{Fe}_2\text{O}_3$  clusters. Because of the lack in experimental data for neutral  $\text{Fe}_x\text{O}_y$  clusters, the spin state of  $\text{Fe}_2\text{O}_{1-3}$  model clusters was defined through the test of different

$\text{C}_{2v}$   $\text{Fe}_2\text{O}_{1-3}$  conformers with different spin multiplicities. The conformers with the lowest electronic energy were chosen for further calculations. The spin conversion which is known to be important in many reaction systems involving transition metals [10,15] has not been employed in current study and is the subject of further investigations. Thus, we assume that the spin of the molecules preserves along the course of reaction. The reaction pathways are studied for  $\text{Fe}_2\text{O}_{1-3} + \text{CO} \rightarrow \text{Fe}_2\text{O}_{1-2} + \text{CO}_2$ , and  $\text{Fe}_2\text{O}_{1-3} + \text{H}_2 \rightarrow \text{Fe}_2\text{O}_{1-2} + \text{H}_2\text{O}$ . Additional pathways are followed for  $\text{Fe}_2\text{O}_3 + \text{CH}_4 \rightarrow \text{F}_2\text{O}_2 + \text{CO} + 2\text{H}_2$ , and  $\text{Fe}_3\text{C} + \text{CO}_2 \rightarrow 3\text{Fe} + 2\text{CO}$ . The reaction pathway calculations involve geometry optimizations of various reaction intermediates and transition states through which the intermediates transfer to each other. The transition state optimizations are performed by employing the either Berny algorithm [16] or the synchronous transit-guided quasi Newton (STQN) method [17]. Vibrational frequency calculations are performed to check that reaction intermediates and transition state species have zero and one imaginary frequencies, respectively. The hybrid  $\omega\text{B97XD}$  exchange-correlation functional [18] which includes empirical dispersion is used. The basis set adopted is the balanced polarized triple-zeta def2tzvp basis set [19]. We believe, that the used long-range-corrected hybrid functional,  $\omega\text{B97XD}$  accounts for the strongly correlated d-electrons of iron-oxide clusters, because it is shown to perform well in the comprehensive thermochemical benchmark set of metal organic reactions [20]. The studied reaction pathways are presented in the form of energy diagrams. Cartesian coordinates and energies ( $E_{\text{elec}}$ ,  $H_0\text{ K}$ ,  $H_{298\text{ K}}$ , and  $G_{298\text{ K}}$ ) for all of the optimized structures (intermediates and transition states) are listed as Tables S1–4 in the Supporting Information. The relative free energies of the adducts and intermediates, shown on the diagrams were calculated under standard conditions (298.15 K, 1 atm) and represent the standard free energy change of the corresponding reaction, as  $\Delta G^{\circ}(\text{rxn}) = \sum \Delta G_f^{\circ}(\text{products}) - \sum \Delta G_f^{\circ}(\text{reactants})$ .

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2018.07.027>.

## 3. Computational results

To test the validity of the  $\omega\text{B97XD}/\text{def2tzvp}$  method for calculation of reaction pathways for multicycles of CO and  $\text{CH}_4$  oxidation by  $\text{Fe}_x\text{O}_y$ , the bond dissociation energies ( $D^{\circ}$ ) and the bond lengths ( $r_b$ ), are calculated and compared with experimental values for CO,  $\text{CH}_4$ , and FeO molecules. We used set of pure generalized gradient approximation functionals, GGA (BP86 [21] and PBE [22]), meta-GGA functional (TPSS [23]) and dispersion corrected range separated hybrid functional ( $\omega\text{B97XD}$  [18]). The bond dissociation energy  $D^{\circ}$  for a bond A–B which is broken through the reaction  $\text{AB} \rightarrow \text{A} + \text{B}$  is defined here as the standard-state enthalpy change for the reaction at a 298.15 K. That is,  $D^{\circ} = \Delta H_f^{\circ}(\text{A}) + \Delta H_f^{\circ}(\text{B}) - \Delta H_f^{\circ}(\text{AB})$ , where  $\Delta H_f^{\circ}$  is the standard-state heat of formation. The comparison is given in Table 1.

The  $\omega\text{B97XD}$  functional shows excellent performance for bond length (within 0.02 Å) calculations. This functional little underestimates  $D^{\circ}$  of CO and  $\text{CH}_4$  by 0.19 and 0.12 eV, respectively. The  $D^{\circ}$  value of FeO calculated through the  $\omega\text{B97XD}$  functional is greater than experimental value by 0.09 eV. That is expected since in the simplest case where the bond of a diatomic molecule is broken,  $D^{\circ}$  at 298 K is greater than  $D^{\circ}$  at 0 K by an amount which lies between RT and (3/2) RT (i.e. 0.03–0.04 eV). We expect that the relative energetics for multicycles of CO and  $\text{CH}_4$  oxidation by  $\text{Fe}_x\text{O}_y$ , can be reasonably predicted by  $\omega\text{B97XD}/\text{def2tzvp}$  since the calculated  $D^{\circ}$  value of FeO is accurate enough. The BP86 functional, which has a good performance for electron affinity calculations, overestimates  $D^{\circ}$  values, and the largest error (>1 eV) occurs for

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