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A density functional theory study on the effect of silica support: Methane activation on nickel oxide clusters through a radical mechanism

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ABSTRACT

Supported transition metal catalysts belong to an important family of catalyst in chemical industry, making the support effect to be a important issue in fundamental research. A theoretical computation using density functional theory (DFT) was performed to investigate the support effect of a silica model on the initial step of methane activation on Ni_xO_x (where, $x = 2, 3$) clusters. The behavior of four reactions were studied by exploring their potential energy surfaces (PES), namely, (i) CH_4 reacting with an unsupported Ni_2O_2 cluster, (ii) with a silica-supported Ni_2O_2 cluster, (iii) with an unsupported Ni_3O_3 cluster, and (iv) with an silica-supported Ni_3O_3 cluster. For each of these four reactions, only a radical mechanism was investigated, and the PESs with different spin states were explored. A spin transition process is involved for the reactions on the unsupported Ni_xO_x clusters, and no spin transition is required for the case of supported Ni_xO_x clusters. The reaction barrier as well as the reaction free energy is increased with the involvement of the model silica support. These results provide a deeper insight into the support effect on the C—H bond activation of small alkanes in general and of methane in particular on supported transition metal catalysts.

1. Introduction

Methane (CH_4) is the most abundant hydrocarbon in nature. The C—H bond activation of CH_4 in particular and of light alkanes in general on a solid catalyst is a key step in the catalytic conversion of light alkanes [1,2]. Activation of the C—H bond of CH_4 has been studied extensively on transition metal oxides and transition metal complexes. Many studies on CH_4 activation on transition metal complexes focused on better understanding the mechanisms of C—O/C—N/C—C bond formations involved in organic synthesis using transition metal catalysts. For example, Sun et al. [3] reported an equatorial ligand effect on the C—H bond activation of CH_4 on a non-heme Fe(IV)–oxo complex. The reaction channels of σ- and π- and a mixing pathway were found when H approaches the Fe=O group. Nakamura et al. [4] reported the C—H bond activation of CH_4 on a Rh–carbene complex and the carbene insertion into the C—H bond was found to be achieved in one elementary step. For CH_4 activation on a solid surface, Zhang et al. [5] reported CH_4 activation on a $CaSO_4$ surface. The mechanism for the first reaction step is a radical mechanism in which the CH_3 radical is produced. Liu et al. [6] investigated complete decomposition processes of CH_4 on mono- and bimetallic surfaces such as Fe, Ni and NiCo. A spontaneous formation of metal-CH_3 and metal-H species was investigated for the initial decomposition of CH_4.

Compared to the transition metal complexes which are usually used in homogeneous catalysis, supported transition metal oxides are often used in important industrial processes such as the reforming of alkanes, the selective oxidation of alkanes, hydrodesulfurization and other processes [7]. In particular, supported Ni-based catalysts are often used in processes like CH_4 reformation [8], hydrogenation of alkenes [9] and Fischer–Tropsch reactions [10]. Using a catalytic support usually leads to a lower cost of the transition metal as well as a higher stability of the catalytic material than using catalysts without catalytic supports. However, the role of a catalytic support in catalytic reactions is poorly understood, especially at the molecular level [11]. In

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particular, the reports on understanding the role of a catalytic support during the catalytic reactions involving CH_4 and transition metal oxides are sparse.

This paper reports a density functional theory (DFT) study of the C—H bond activation of CH_4 on both unsupported and silica-supported Ni_xO_x (where $x = 2, 3$) clusters. We examine how reaction behavior changes (instead of the detailed reaction mechanisms) without and with the involvement of a model silica support. Although the results from state-of-the-art DFT computations may be hard to provide a quantitative explanation of experimental data like the reaction barrier or the reaction rate, the DFT calculated relative reaction barrier is much more credible and reliable [12]. On the other hand, there may be a large gap between the catalytic model and the real prepared catalyst [13] and this makes the qualitative explanation of the experimental data harder to obtain. Therefore, this work only seeks to elucidate a qualitative and general understanding of the support effect for the C—H bond activation of light alkanes on supported transition metal oxides instead of a quantitative explanation of the experimental data.

The initial activation of light alkanes on transition metal surface may undergo with a radical mechanism [3,5,6,14,15] or a concerted mechanism [4,14]. For CH_4 in particular, many researchers prefer a radical mechanism especially on heterogeneous catalysts [5,6]. Since the aim of this paper is to elucidate the support effect rather than the detailed reaction mechanism, only the support effect on the C—H bond activation of CH_4 through a radical mechanism is investigated.

2. Computational methods

The structures and energetic of four reactions were investigated with DFT calculations in this work, and they are:

CH_4 + an unsupported Ni_2O_2 cluster	(Rxn.i)
CH_4 + a model silica supported Ni_2O_2 cluster	(Rxn.ii)
CH_4 + an unsupported Ni_3O_3 cluster	(Rxn.iii)
and	
CH_4 + a model silica supported Ni_3O_3 cluster	(Rxn.iv)

respectively. The DFT calculations were performed by using the hybrid B3LYP [16–18] exchange and correlation functionals to explore the PESs of the reactions of CH_4 with unsupported Ni_xO_x (where $x = 2, 3$) clusters and with silica-supported Ni_xO_x clusters through a radical mechanism. B3LYP is known to provide a good description of the PES for transition metal oxide clusters [19,20]. The 6-311G(d,p) basis set was used for the C, H, and O atoms in the CH_4 and Ni_xO_x parts of the system of interest and the 6-31G basis set was used for all the Si, H, and O atoms in the model silica part of the system of interest. The modified 6-31G(d) (m6-31G*) was used for the Ni atoms [21]. Five component *d* functions were employed in the calculations. These combined basis sets were denoted as BS1 in this paper. We found it is quite difficult to achieve convergence for the self-consistent field (SCF) calculation for the nickel oxide clusters in spite of several different functionals other than B3LYP being tried. The quadratic convergence algorithm was used to achieve the SCF convergence, which makes the SCF calculation very time-consuming, especially for the supported Ni_2O_2 and supported Ni_3O_3 systems. Since this work aims at a qualitative understanding on the support effect, only B3LYP/BS1 level of theory was used.

All PESs were explored by optimizing the geometries in the energy minimums for the reactants and the products, and the first-order saddle points for transition states using the Gaussian 09 program suite [22] (B.01 version). All of the atoms in CH_4, Ni_xO_x clusters and the model silica support, are allowed to relax during the structure optimizations. The notations having the form of **[R/TS/P]-n** will be used in the later sections, where **R/TS/P** represents reactants, transition state or products, and **n** represents one of i–iv for the Rxn. numbers defined above. For example **R-ii** represents the reactants of Rxn.ii, and **TS-iii** represents the transition state of Rxn.iii.

Frequency analyses were performed to confirm the energy minimums and the first-order saddle points, as well as to obtain the zero-point corrected energies (ZPE), entropies and free energies (at 873.15 K) of the optimized geometries. For easy comparisons, only the relative free energy (in kcal/mol) of the optimized geometries will be presented in the paper hereafter, with the free energy reference using the ground state of the reactants for each reaction. The calculated free energy for reach geometry can be seen in the Supporting Information. Intrinsic reaction coordinate (IRC) computations [23] were performed to confirm that the transition states connected the appropriate reactants and products.

3. Results and discussion

3.1. CH_4 activation on an unsupported Ni_2O_2 cluster

3.1.1. The reactants

The results reported in our previous studies [24,25] showed that several first-row transition metal loaded Y zeolites (M/Y) may have quite small clusters since no features relating to M were observed from their XRD patterns while the elemental analysis results showed significant metal loadings. The *ex-situ* extended XAFS study showed that the Ni components in Ni/H–Y existed in nanoparticles in the form of Ni_mO_n (n is smaller but close to m), when Ni/H–Y was exposed to a mixture of ethane, O_2 and He. Since this paper focuses on understanding the support effect of silica instead of the size and chemical status of the nanoparticle, only Ni_xO_x ($x = 2, 3$) clusters were used to model the nickel oxide clusters.

Panels a and b in Fig. 1 show the optimized geometries of the reactants of CH_4 and unsupported Ni_2O_2 (in triplet and quintet states), respectively. It is interesting to note that the gaseous Ni_2O_2 cluster can be produced in a matrix-isolation experiment and has been characterized by infrared spectroscopy [26,27]. Gaseous Ni_2O_2 has a cyclic structure and Ni—O bond lengths of ~180 pm that are consistent with results from B3LYP/BS1 level of theory calculations reported in this work.

3.1.2. The selection of PESs with different spin state for the reaction system

Nickel-based compounds may have more than one accessible spin states [28,29]. Since the reaction system of interest in this work have even number of electrons, the spin multiplicity (S) of the reaction system should be 1, 3, 5, 7, etc. (corresponded to the PES of singlet, triplet, quintet, heptet, etc.). A superscript is used before a species name to represent the spin multiplicity of this species in this paper. For example, $^5Ni_2O_2$ is the quintet Ni_2O_2. The optimized geometry in the nonet state ($S = 9$) was not found in spite of several attempts for all of the Ni_xO_x clusters studied in this work, therefore the nonet PES and the PESs with larger S were not considered for all of Reactions i–iv. Then the reaction on the singlet PES was also rule out, since the initial products of CH_4 activation through a radical mechanism are two radicals, each of which has an S of 2. In addition, $^1Ni_2O_2$ is unfavorable over $^5Ni_2O_2$ by 22.5 kcal/mol in free energy for the unsupported case, and by 18.2 kcal/mol for the supported case, and $^1Ni_3O_3$ is unfavorable over $^7Ni_3O_3$ by 53.1 kcal/mol for the unsupported case, and by