Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 247 (2007) 119–126
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

A DFT study of the mechanism and kinetics of methane oxidation to formaldehyde occurring on silica-supported molybdena

Shaji Chempath, Alexis T. Bell *

Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462, USA

Received 14 September 2006; revised 10 January 2007; accepted 12 January 2007

Abstract

A theoretical analysis was carried out of the mechanism and kinetics of methane oxidation to formaldehyde occurring on isolated molybdate species supported on silica. Both mono-oxo and di-oxo molybdate structures were used to represent the active centers. The energetics for each elementary reaction was determined from density functional theory calculations, and the entropy changes were determined from calculations based on statistical mechanics. The results of this analysis show that the mechanism based on di-oxo molybdate species agrees more closely with observed rates of methane oxidation than that based on mono-oxo molybdate species. It is also found that the formation of formaldehyde occurs via the reaction of methane with peroxide species formed via the adsorption of O_2 on reduced Mo^{IV} centers. The extent of Mo^{VI} reduction to Mo^{IV} is well under 1% under reaction conditions, in good agreement with experimental observations.

Keywords: Quantum chemistry; Peroxide; MoO_x; Methane activation; CH_2O

1. Introduction

Silica-supported molybdena is known to be a highly active catalyst for the direct oxidation of methane to formaldehyde [1–7]. The effectiveness of silica is ascribed to the minimal decomposition of CH_2O on this material relative to other support oxides. It is also notable that for Mo surface concentrations below ∼1 Mo/nm^2, the turnover frequency for methane oxidation is independent of molybdena surface concentrations [2,4]. Because virtually all of the molybdena at such low surface densities is present as isolated molybdate species [8–17], this means that such species are active for the oxidation of methane to formaldehyde.

The mechanism and kinetics of methane oxidation to formaldehyde have been investigated by a number of authors [7,18–22]. In most of these studies, it is assumed that two O atoms, each associated with a single Mo atom, are involved in the formation of CH_2O and H_2O, and that reoxidation of the catalyst by O_2 restores one O atom per Mo. This sequence is represented by

$$CH_4 + 2Mo{=}O \rightarrow CH_2O + H_2O + 2Mo,$$
$$2Mo + O_2 \rightarrow 2Mo{=}O.$$

Although such simple schemes have been used successfully to describe the kinetics of methane oxidation [6,7,21], they are inconsistent with a number of physical observations. For example, the degree of reduction from Mo^{VI} to Mo^{IV} determined from such redox models of the mechanism is projected to be 10–20% [6,7], whereas experimental evidence suggests that the degree of reduction is <1% [22,23].

It is also difficult to understand how isolated molybdate species could catalyze the oxidation of CH_4 if O atoms from two completely isolated molybdate species are required. The incorporation of O atoms from molecular oxygen into reduced Mo sites is equally unexplained for this case. Further evidence against the formation of CH_2O via CH_4 reduction of Mo=O bonds associated with isolated molybdate species has come from pulse reaction studies [24]. Such experiments have shown that a pulse of CH_4 without O_2 reacts to a much smaller extent than does a pulse of CH_4 including O_2. The difference between the two experiments has been used to suggest that a metastable

* Corresponding author. Fax: +1 510 642 4778.
E-mail address: bell@cchem.berkeley.edu (A.T. Bell).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2007.01.012

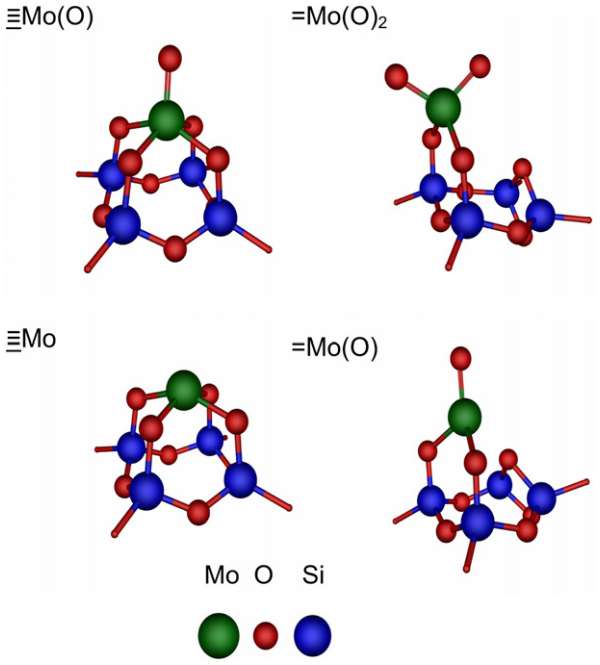

Fig. 1. Geometries of MoO_x anchored on silica. ≡Mo(O) and =$Mo(O)_2$ represent $Mo^{VI}O_x$ species while ≡Mo and =Mo(O) represent $Mo^{IV}O_x$ species.

form of oxygen exists that is incompletely reduced. This view is also supported by surface potential measurements [25,26] made under various CH_4 and O_2 partial pressures, which suggest that the form of oxygen involved in CH_4 oxidation is reduced by one electron per O atom. Building on these observations as well as their own, Ohler and Bell [22] proposed that CH_4 is oxidized by peroxide species formed by the reaction of O_2 with a small concentration of reduced molybdate species. In the first step of their mechanism, CH_4 adds across the peroxide to form an $Mo(OH)(OCH_3)$ species. Formaldehyde is then formed via the transfer of a hydrogen atom from the methoxide to the hydroxyl group. Desorption of formaldehyde and water lead to the final products.

Quantum mechanical investigations can provide information that is complementary to that obtained from experimental studies. Chempath et al. [27] recently reported a density functional theory (DFT) investigation of the structure of isolated molybdate species and compared their findings with experimental evidence obtained from Raman, XANES, and EXAFS observations [23]. They considered two possible modes of Mo^{VI} molybdate species bonded to silica: one with four Mo–O–Si linkages and another with two Mo–O–Si linkages. In the present paper, these modes are designated ≡Mo(O) and =$Mo(O)_2$, respectively (see Fig. 1). Their work demonstrated convincingly that isolated molybdate species are present as di-oxo, =$Mo(O)_2$, structures rather than mono-oxo, ≡Mo(O), structures after calcination of highly dispersed silica-supported molybdena (0.44 Mo/nm^2) at 920 K. H_2 reduction of =$Mo(O)_2$ was predicted to form =Mo(O), in good agreement with what has been observed experimentally by Raman and EXAFS.

Fu et al. [28] used DFT to examine the energetics of CH_4 oxidation using a Mo_3O_9 cluster to model supported MoO_x. In this model, each molybdenum has two Mo=O bonds and methane directly reacts with the Mo=O bonds to form a =$Mo(OH)(OCH_3)$ species, in which hydroxyl and methoxide groups are attached to the Mo(IV) cation. The overall free energy barrier at 873 K for direct methane activation by the Mo=O bonds is estimated to be 75.6 kcal/mol. The subsequent steps leading to formation of CH_2O and H_2O and the mechanism by which Mo^{IV} is reoxidized to Mo^{VI} were not considered.

The aim of the present investigation was to explore the plausibility of the reaction mechanism proposed by Ohler and Bell [22] for the oxidation of CH_4 to CH_2O occurring on isolated silica-supported molybdate species. Toward this end, DFT calculations were carried out using small molecular clusters to represent the elementary processes occurring on ≡Mo(O) and =$Mo(O)_2$. Particular attention was given to calculations of the thermodynamics of Mo^{VI} to Mo^{IV} reduction and the activation of methane by peroxide species formed by O_2 adsorption on structures containing Mo^{IV}. The equilibrium constants and rate coefficients determined in the course of this study were then used to predict the rate of methane oxidation for different temperatures and partial pressures of CH_4 and O_2. The ultimate goal of this work was to establish whether the overall rate of reaction occurring via ≡Mo(O) or =$Mo(O)_2$ is faster.

2. Theoretical methods

Silica-supported molybdate species were represented by the structures shown in Fig. 1. These models were chosen based on our previous study of the structure of MoO_x species on different cluster representations of a silica surface [27]. In that study, we found that an accurate representation of the energetics of Mo oxidation and reduction could be achieved using clusters containing four silicon atoms. Calculations with larger models gave similar energetics and vibrational frequencies to those obtained with the four-silicon model but at the expense of significantly higher computational time. For this reason, we have represented the surface of silica as a ring of four Si atoms connected together by four O atoms with the remaining valences of Si terminated by Si–OH groups. The Mo^{VI} molybdates were taken to be in the form of either mono-oxo [≡Mo(O)] or di-oxo [=$Mo(O)_2$]. Both structures are identical to those in our previous study. As noted in the Introduction, we recently showed that the Raman spectrum and EXAFS pattern of the di-oxo structure agree closely with those observed experimentally for isolated molybdate species supported on silica after calcination at 920 K [27]. The reason for considering both mono- and di-oxo structures in the present study is that our previous work has shown that these structures can co-exist, depending on the partial pressure of water and the temperature.

Electronic energies of reactant, product, and transition states were determined using DFT. The B3LYP functional was used to describe electron exchange and correlation. The geometry of ground-state and transition-state structures were optimized using the 6-31G* basis set. The LANL2DZ effective-core potential was used to describe the Mo atom. Molybdate species bonded to silica were treated as freestanding clusters. All of the atoms in the cluster were allowed to relax during the geome-