

Cluster quantum-chemical study of the chemisorption of methane on zinc oxide surface

N.U. Zhanpeisov^b, G.M. Zhidomirov^b, M. Baerns^{a,*}

^a *Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*

^b *Institute of Catalysis, 630090 Novosibirsk, Russia*

Received 9 February 1994; revised 17 August 1994; accepted 7 February 1995

Abstract

A quantum-chemical study based on a supermolecular approach and using a modified MINDO/3 method was applied to study the interactions of methane (a) with a ZnO surface containing structural defects i.e., low-coordinated $\text{Zn}_{\text{LC}}^{2+}$ and $\text{O}_{\text{LC}}^{2-}$ ions and (b) with dioxygen preadsorbed on various oxygen vacancies of the ZnO surface. The zinc oxide was modelled by a $\text{Zn}_{16}\text{O}_{16}$ four-layer molecular cluster. From calculated heats of dissociative adsorption of CH_4 on the various pairs of acid–base centres of the ZnO surface it could be derived that only the $\text{Zn}_{2\text{C}}^{2+}-\text{O}_{3\text{C}}^{2-}$ pair of centres is responsible for initial activation of methane. The calculations also indicate that for dioxygen, molecular adsorption on the oxygen vacancy centres is more favourable than dissociative adsorption. On the basis of computational results the various channels of methane interaction with zinc oxide, the possibilities of formation of various oxygen vacancies on ZnO and their role in activation of dioxygen and methane molecules are discussed.

Keywords: Chemisorption; Methane; Oxide surface; Quantum-chemical study; Zinc

1. Introduction

ZnO is an n-type semiconductor and has a catalytic activity in olefin hydrogenation, CO oxidation, syngas conversion to methanol, higher linear and higher branched alcohols, etc., as is well known [1–5]. Among the modern spectroscopic techniques, theoretical quantum chemical methods are also used to study the interaction of ZnO with the reactants – although these methods are limited to a qualitative description of these phenomena for small molecules only [6–11]. Thus, for example, Morimoto et al. [6,7] investigated the electronic structure of polar (0001) and non-

polar (10 $\bar{1}$ 0) surfaces of ZnO by the DV- X_α method. Earlier, the same type of molecular orbital calculations based on a ZnO_4^{6-} cluster model have been performed by Tossel [8] and by Gopel et al. [9] using empirically fitted tight-binding band calculations. Anderson et al. [10] have reported on the electronic structure of bulk and surface ZnO, the surface relaxations and the adsorption of a CO molecule on the (10 $\bar{1}$ 0) non-polar ZnO surface using the ASED-MO method. Nakatsuji et al. [11] studied the interactions of a hydrogen molecule with a (10 $\bar{1}$ 0) ZnO surface by an ab initio method with and without a Madelung potential modelled by the 32 point charges of $q = \pm 0.5$ e.u. situated on the first and second layers.

* Corresponding author.

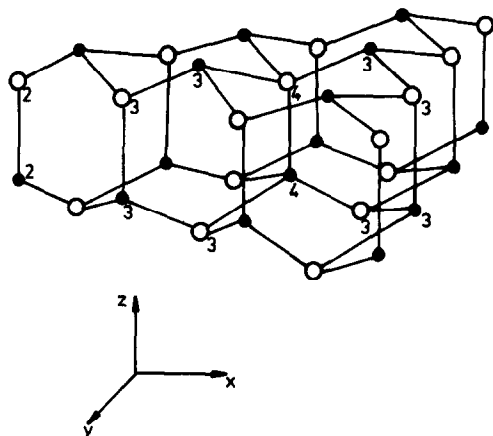


Fig. 1. $Zn_{16}O_{16}$ molecular cluster used as a model of zinc oxide. The polar $(000\bar{1})$ surface is the same as the (0001) surface with Zn and O interchanged. Numbers correspond to the degree of coordination (LC) of cations and anions. Symbols: ● Zn_{LC}^{2+} , ○ O_{LC}^{2-} .

In the present paper results are reported on quantum chemical cluster calculations by a modified MINDO/3 method for the adsorption of a CH_4 molecule on pure ZnO and on ZnO oxygen vacancies on which dioxygen molecules are preadsorbed. Based on these calculations the mechanism of activation of methane via heterolytic dissociative or homolytic adsorption on pure zinc oxide, the possibility of formation of various oxygen vacancies on ZnO and their role in activation of dioxygen and methane molecules are discussed.

2. Method of calculation and surface model

Cluster quantum chemical calculations were performed within the framework of the MINDO/3 method; its parameterization extended for studying Zn-containing compounds [12]. The ZnO surface was modelled by $Zn_{16}O_{16}$ representing a four-layer molecular cluster (Fig. 1). This choice of molecular model allows us to analyse the participation of all types of low-coordinated acid-base centres (Zn_{LC}^{2+} and O_{LC}^{2-} ions) in the adsorptive interaction. As was shown in previous papers [13,14], the size of the $Zn_{16}O_{16}$ cluster is considered to be large enough to ascertain that any further growth of its size does not affect the optimal

geometry and chemisorption properties of various similar surface characteristics (e.g., corners, edges, faces, etc.). This conclusion is based on systematic calculations of zinc oxide clusters modelled by Zn_4O_4 , $Zn_{10}O_{10}$, $Zn_{13}O_{13}$, $Zn_{16}O_{16}$ and $Zn_{25}O_{25}$. Thus, for example, the main experimental properties of a ZnO crystal is presented by this $Zn_{16}O_{16}$ molecular cluster [14]. In the $(000\bar{1})$ surface the optimized bond distance of Zn–Zn and of O–O in the $(000\bar{1})$ surface amount to 3.354 and 3.317 Å, respectively. The optimized bond distance of Zn–Zn in non-polar $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces are equal to 5.297 and 5.517 Å, respectively. The experimental values corresponding to these situations are equal to 3.25 (instead of 3.354), 3.25 (3.317), 5.21 (5.297) and 5.63 (5.517) Å according to [15,16]. The variations of the coordination number is only slightly influenced by the charge changes of the Zn_{LC}^{2+} and O_{LC}^{2-} ions.

The Madelung field i.e., the influence of aside part of the crystal lattice on separate $Zn_{16}O_{16}$ cluster in a pure ionic-structure approach has not been taken into account. In the applied supermolecular approach the inclusion of the Madelung potential should not result in any essential distortion of the results calculated. Moreover, it is known [17,18] that the Madelung field is higher on the bulk compared to the surface and leads to a decrease of ionicity and to an increase of covalent binding of surface-chemisorbed complexes. This was demonstrated earlier [14] when studying the adsorption of a CO molecule on $(000\bar{1})$ polar surface of ZnO. This latter situation was modelled by using (a) a $Zn_{16}O_{16}$ molecular cluster, (b) a $Zn_{16}O_{16}$ molecular cluster with 18 point charges situated at the nearest positions of Zn_{LC}^{2+} and O_{LC}^{2-} ions in the perpendicular directions compared to CO adsorption, and (c) a small ZnO_3^{4-} cluster embedded in a lattice of 1038 point charges which correctly represent the half-infinite ionic crystal. The results of the calculations have practically not changed. This is in favour of significant localization of the chemical interactions in the studied oxide surface.

3. Results and discussion

It is well known from experimental evidence that zinc oxide is catalytically active in converting methane to carbon oxides but it is unselective for its oxidative coupling to C₂ hydrocarbons. From a theoretical point of view there are two different channels for the interaction of the methane molecule with the ZnO surface; this may be either heterolytic dissociative adsorption on acid–base pairs of centres or homolytic splitting with the formation of surface hydroxyl group due to hydrogen atom abstraction. In the latter case methyl group formed is passed on to gas phase. In the former case effective charge distributions on the adsorbed fragments are assumed which correspond to the formation of a metal–methyl and a hydroxyl group or a metal–H and an alkoxide group, respectively (reactions 1 and 2).



For these alternatives calculations with a full optimization of the geometry of the chemisorbed complexes have been performed, i.e. taking into account relaxations of the active centres on the oxide surface due to a response to the adsorbed particle interactions. Calculated energies of various adsorption forms are shown in Table 1. From these results it is clear that only dissociative chemisorption of the methane molecule via the formation of a metal–methyl bond is more favourable by energetics than the two other ones. It should be noted that a homolytic channel differs from the heterolytic one by the nature of the final state of the chemisorbed complex; the former case corresponds to the radical state (formation of a surface hydroxyl group only) while the latter case results in a non-radical state. The maximum gain in chemisorption energy takes place when Zn_{2C}²⁺–O_{2C}²⁻ acid–base pairs act as the centres of localization of the fragments of the dissociated molecule. Evidently, the quantity of such paired centres on the ZnO surface should be very small [13]. Hence, the adsorption on the statistically more preferable

Table 1

Energies (*E*) of methane adsorption on various pairs of acid–base centres (heterolytic adsorption) and on basic centres only (homolytic adsorption) as calculated by the MINDO/3 method

Type of centre	ΔE^a kcal mol ⁻¹
<i>Heterolytic adsorption</i>	
Zn _{3C} ²⁺ –O _{3C} ²⁻	–29.6
Zn _{3C} ²⁺ –O _{2C} ²⁻	–10.4
Zn _{2C} ²⁺ –O _{3C} ²⁻	2.8
Zn _{2C} ²⁺ –O _{2C} ²⁻	23.6
Zn _{4C} ²⁺ –O _{3C} ²⁻	–41.2
Zn _{3C} ²⁺ –O _{3C} ²⁻	–80.7 ^b
Zn _{3C} ²⁺ –O _{2C} ²⁻	–40.5 ^b
<i>Homolytic adsorption</i>	
O _{3C} ²⁻	–46.9
O _{2C} ²⁻	–33.3

^a Positive value corresponds to stabilization upon adsorption.

^b These values correspond to heterolytic dissociative chemisorption of methane by reaction (2), see text.

Zn_{2C}²⁺–O_{3C}²⁻ ion pairs should be responsible for initial activation of methane (Table 1). The dissociative adsorption of methane on a polar (0001) ZnO surface is energetically not favourable with an increase in the coordination number of nearest bulk Zn_{4C}²⁺ up to a value of 5 (see Table 1). This latter case corresponds to the interaction of a methyl fragment formed by bulk Zn_{4C}²⁺ via the centre of gravity of three nearest surface oxygens.

The heterolytic dissociation leads to a noticeable polarization of the molecule fragments which are chemisorbed. Thus, for example, we obtained the following effective charge distribution upon adsorption of a methane molecule on Zn_{2C}²⁺–O_{3C}²⁻ ion pairs: $q_{\text{CH}_3} = -0.125$ e.u. (methyl fragment on Zn_{2C}²⁺) and $q_{\text{H}} = +0.259$ e.u. (hydrogen on O_{3C}²⁻). The optimized geometry of such a chemisorbed complex is shown in Fig. 2. It is clear that upon adsorption of the CH₄ molecule the Zn_{2C}²⁺ and O_{3C}²⁻ ions are substantially moved from their optimal positions within the non-interacting cluster to the direction of adsorbed fragments.

The formation of oxygen vacancies on ZnO is considered to occur upon adsorption of slightly acidic H₂ or CH₄ and subsequent dehydration of the zinc oxide surface. As was shown above for the CH₄ molecule its dissociative adsorption on Zn_{2C}²⁺–O_{2C}²⁻ acid–base pairs is more favourable

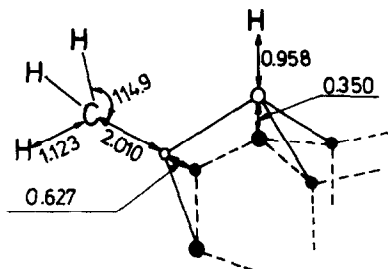
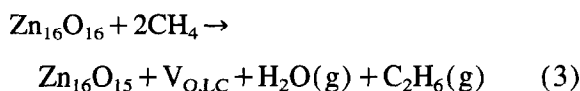


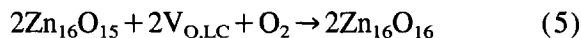
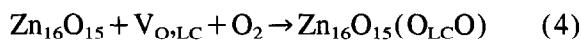
Fig. 2. Structural data of the dissociatively chemisorbed methane molecule on $Zn_{2C}^{2+}-O_{3C}^{2-}$ acid-base pair centres. (Bond lengths in Å, bond angles in degrees). The dotted line corresponds to the optimal positions of ions in the molecular cluster not interacting with methane. Symbols: ● Zn_{2C}^{2+} , ○ O_{3C}^{2-} .

than on other pairs. If one assumes that a second CH_4 molecule is dissociatively adsorbed on the same O_{2C}^{2-} centre and on another nearest Zn_{3C}^{2+} acid centre as the first one, a precursor of a water molecule is formed. When the water molecule is removed and two methyl radicals dimerize to ethane, either on the surface or most probably in the gas phase after desorption, an oxygen vacancy ($V_{O,2C}$) is formed; this process is slightly favourable by energetics (the gain in energy is equal to 5.8 kcal/mol which is calculated as the difference in total energies between the sum of an oxygen vacancy ($V_{O,2C}$) containing cluster, water and ethane molecules and the sum of non-interacting initial cluster and two methane molecules). The overall chemical process is shown by Eq. (3):



The formation of an oxygen vacancy $V_{O,3C}$ from a water precursor on threefold-coordinated O_{3C}^{2-} ($V_{O,3C}$) is not favourable by energetics (-24.5 kcal/mol). Of course, if a $V_{O,2C}$ vacancy exists then the corresponding $V_{O,3C}$ can be formed via a consecutive exchange reaction on the lattice of the oxide surface at high temperatures i.e., an exchange reaction is assumed to occur between a vacancy and the nearest threefold-coordinated surface oxygen. On an oxygen vacancies a dioxygen molecule from the gas phase is easily activated. According to the calculations, molecular adsorption of a dioxygen molecule on such a vacancy (Eq. 4) is more favourable by energetics

than dissociative adsorption according to Eq. 5; (for energetics see Table 2).



In the latter case the initial state of the surface is recovered. The sum of the negative atomic charges on molecularly adsorbed dioxygen on $V_{O,3C}$ is equal to -0.645 e.u. On a dioxygen molecule adsorbed on a vacancy centre dissociative adsorption of a methane molecule can easily occur via the formation of a metal-methyl fragment and hydrogen peroxide group. For example, the energy of such dissociative adsorption of a methane molecule on Zn_{3C}^{2+} and on dioxygen adsorbed on $V_{O,3C}$ is equal to 5.5 kcal/mol.

The other two reaction channels i.e., heterolytic dissociative methane adsorption via direct formation of a methyl peroxide group and a metal-hydrogen fragment or homolytic splitting of a C-H bond of methane via abstraction of a hydrogen atom by the dioxygen group, turn out to be unfavourable by energetics (-34.6 and -20.2 kcal/mol, respectively). Comparable results are also obtained for the adsorption of methane on Zn_{3C}^{2+} and on $V_{O,2C}$ occupied with a preadsorbed dioxygen molecule ($Zn-CH_3/OOH$: 7.1, $Zn-H/OO-CH_3$: -20.1 and $OO-H$: -13.8 kcal/mol, respectively). These results show that direct formation of O-C fragments via dissociative adsorption of the methane molecule on $V_{O,3C}$ containing an adsorbed dioxygen molecule is not favoured by energetics.

Table 2
Adsorption energies (ΔE) of a dioxygen molecule on low-coordinated oxygen vacancy centres calculated by the of MINDO/3 method

Type of vacancy	Reaction ^a number	ΔE ^b kcal mol ⁻¹
$V_{O,3C}$	4	38.5
$V_{O,3C}$	5	20.3
$V_{O,2C}$	4	26.4
$V_{O,2C}$	5	-4.6

^a See text.

^b Positive value corresponds to stabilization upon adsorption.

The results presented above do not explain the direct non-selective conversion of methane to CO_x on ZnO catalysts. Thus, it has to be assumed that methyl species either still located on the ZnO surface or already desorbed into the gas phase react non-selectively with gas phase oxygen via a peroxy radical to CO_x .

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft (Graduiertenkolleg 'Dynamic Processes on Surfaces'). N.U.Z. thanks DFG for a grant for staying at Ruhr-Universität Bochum.

References

- [1] A.L. Dent and R.J. Kokes, *J. Phys. Chem.*, 73 (1969) 3773.
- [2] R.J. Kokes, *Acc. Chem. Res.*, 6 (1973) 226.
- [3] K. Klier, *Adv. Catal.*, 31 (1982) 243.
- [4] P. Courty, D. Durand, E. Freund and A. Sugier, *J. Mol. Catal.*, 17 (1982) 241.
- [5] C.C. Chang and R.J. Kokes, *J. Catal.*, 28 (1973) 92.
- [6] R. Sekine, H. Adachi and T. Morimoto, *Surf. Sci.*, 208 (1989) 177.
- [7] R. Kuwabara, H. Adachi and T. Morimoto, *Surf. Sci.*, 193 (1988) 271.
- [8] J.A. Tossel, *Inorg. Chem.*, 16 (1977) 2944.
- [9] I. Gopel, J. Pollmann, I. Ivanov and B. Riehl, *Phys. Rev. B*, 26 (1982) 3144.
- [10] A.B. Anderson and J.A. Nichols, *J. Am. Chem. Soc.*, 108 (1986) 1385.
- [11] H. Nakatsuji and Y. Fukunishi, *Int. J. Quant. Chem.*, 42 (1992) 1101.
- [12] N.U. Zhanpeisov and G.M. Zhidomirov, *J. Strukt. Khim.*, 33 (1992) 151 (Translated by Plenum).
- [13] N.U. Zhanpeisov, A.G. Pelmenschikov and G.M. Zhidomirov, *Kinet. Katal.*, 31 (1990) 563 (translated by Plenum).
- [14] N.U. Zhanpeisov, G.M. Zhidomirov and M. Baerns, *J. Strukt. Khim.*, 35 (1994) 12 (translated by Plenum).
- [15] S.C. Abrahams and J.L. Bernstein, *Acta Crystallogr. B*, 125 (1969) 1233.
- [16] R.R. Gay, M.H. Nodine, V.E. Henrich, H.J. Zeiger and E.I. Solomon, *J. Am. Chem. Soc.*, 102 (1980) 6752.
- [17] C. Satoko, M. Tsukada and H. Adachi, *J. Phys. Soc. Jpn.*, 45 (1978) 1333.
- [18] M. Tsukada and T. Hoshino, *J. Phys. Soc. Jpn.*, 51 (1982) 2562.