Cluster quantum-chemical study of the chemisorption of methane on a lithium-promoted magnesium oxide doped by zinc oxide

N.U. Zhanpeisov [b], M. Baerns [a],*

[a] Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany
[b] Institute of Catalysis, 630090 Novosibirsk, Russia

Abstract

The reaction of a methane molecule with a lithium-doped magnesium oxide catalyst (Li/MgO) containing small amounts of Zn^{2+} cations (Zn/Li/MgO) was theoretically studied using a modified MINDO/3 method and applying a supermolecular approach. The surface of magnesium oxide (MgO) was modelled by a $Mg_{32}O_{32}$ four-layer molecular cluster containing all types of structural defects i.e., low-coordinated magnesium and oxygen ions (Mg^{2+}_{LC} and O^{2-}_{LC}) of various faces, edges, corners etc. Molecular clusters of lithium-promoted magnesia (Li/MgO) were simulated by isomorphic substitution of Mg^{2+}_{LC} by Li^{+}_{LC}; the excess negative charge of the cluster was compensated by a proton connected to an O^{2-}_{3C} site. For Zn-doped Li/MgO or MgO an isomorphic substitution of Mg^{2+}_{LC} by Zn^{2+}_{LC} was assumed. The calculations indicate that for Zn/Li/MgO or Zn/MgO the substitution of a threefold coordinated magnesium cation by zinc is more favourable by energetics than for four- and five-fold coordinated Mg cations. The computational results are used to interpret the experimentally observed increase of C_{2+} hydrocarbons selectivity in the oxidative coupling of methane when doping a NaOH-promoted CaO catalyst with minor amounts of Zn^{2+} cations.

Keywords: Chemisorption; Lithium-promoted magnesium oxide; Magnesium oxide; Methane; Quantum-chemical study; Zinc oxide

1. Introduction

During the past decade, research work on the oxidative coupling of methane (OCM) to C_{2+} hydrocarbons i.e., preferentially ethylene dealt primarily with the development of suitable catalysts; basic metal oxide containing various dopants appear to be promising [1–5]. Alkali-doped alkaline earth oxides have been frequently used and suggested. Among those catalysts the Li/MgO and Na/CaO systems have been found to be active and highly selective [5–7]. Recently

Baerns and co-workers [8] have observed that C_{2+} hydrocarbon selectivity of a NaOH/CaO catalyst is further increased by adding small amounts of Zn^{2+} cations (0.0001 to 0.1 mol%). To explain this phenomenon it was assumed that Ca^{2+} cations were exchanged by Zn^{2+} cations in the near-surface region forming a pseudo-solid solution. It was suggested that Zn^{2+} acted as an electron acceptor from a carbanion CH_3^- formed in the heterolytic splitting of methane which was subsequently reoxidized by oxygen. This mechanism was, however, only effective as long as there were no zinc oxide clusters on the surface which lead to non-selective methane oxidation.

* Corresponding author.

In the present paper it is attempted to theoretically explain the phenomenon of Zn doping on the basis of results of quantum-chemical cluster calculation on the adsorption of a CH_4 molecule on a zinc-doped Li/MgO catalyst which was assumed to perform similarly to the Na/CaO system. The computational results are based on the modified MINDO/3 method. Previously [9,10] it was shown that the increase of activity of Li/MgO catalyst in comparison with pure magnesium oxide could be explained by using a non-radical molecular cluster for Li/MgO. The same approach was used to explain the influence of Zn_{LC}^{2+} cations of Zn/MgO and for the present Zn/Li/MgO system. It should be noted that the model applied corresponds to electronic neutrality by the nature of the molecular cluster approach. In the study presented below Zn/Li/MgO was used instead of Zn/Na/CaO since the two systems should have similar characteristics, and calculations for Zn/Na/CaO were not possible as the MINDO/3 method did not contain a parameterization for Ca-containing compounds. On the basis of the computational results, the formation of active sites on Zn/Li/MgO and their role in the activation of methane are discussed. It should be emphasized that in the present work no O^- species were observed which might be formed when gas-phase oxygen is adsorbed. This means that methane activation proceeds via heterolytic dissociation of methane on an acid–base pair of centers instead of radical abstraction of a hydrogen atom from methane by a surface O^- species.

2. Method of calculation and surface model

The cluster quantum-chemical calculations were performed within the framework of the MINDO/3 method; its parameterization was extended for studying Zn- [11], Li- [12] and Mg-containing [9] compounds. The MgO surface was modelled by a four-layer molecular cluster $Mg_{32}O_{32}$ (Fig. 1). This choice of a molecular model allows to analyse the participation of all types of low-coordinated acid–base centres
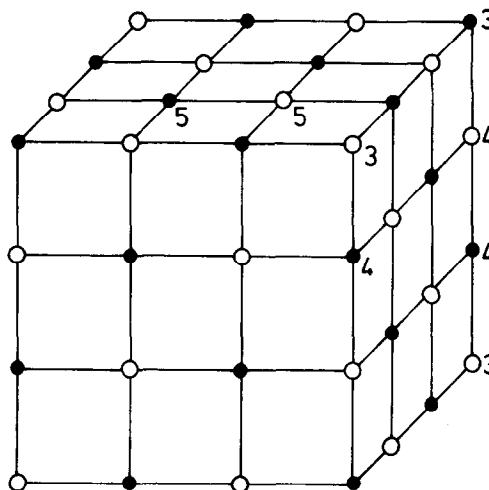

Fig. 1. Four-layer molecular cluster of $Mg_{32}O_{32}$ as model of magnesium oxide. (The numbers correspond to the degree of coordination (LC) of cations and anions. Symbols: ● Mg_{LC}^{2+}, ○ O_{LC}^{2-}.)

(Mg_{LC}^{2+} and O_{LC}^{2-} ions) in the adsorptive interaction with methane. As was shown elsewhere [9,13], the size of the $Mg_{32}O_{32}$ cluster on which the calculations are used is sufficiently large enough i.e., any further growth of its size does not affect the optimal geometry and chemisorption properties of its characteristic surfaces. It should be noted that such a supermolecular approach correctly describes both the relaxation of the various low-coordinated Mg_{LC}^{2+} and O_{LC}^{2-} surface sites and their influence on the energetics of the chemisorptive processes [9,13].

The calculations with respect to the molecular Li/MgO cluster were based on an isomorphic substitution of one Mg_{LC}^{2+} ion by Li_{LC}^+ ion; the resulting excess negative charge of the cluster was compensated by a proton attached to O_{3C}^{2-} [10]. It should be noted that in this case the resulting cluster model corresponds to the neutral and non-radical state. When a zinc cation was incorporated in the surface, Mg_{LC}^{2+} was replaced by isomorphic substitution of Zn_{LC}^{2+}.

The Madelung field i.e., the influence of a side part of the crystal lattice on a separate $Mg_{32}O_{32}$ 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

Table 1
Relaxation (ΔR) of Zn_{LC}^{2+} ions and relative energies ($\Delta\Delta E$) of $Mg_{31}ZnO_{32}$ clusters as calculated by the MINDO/3 method of Zn/MgO when Mg_{LC}^{2+} ions are substituted by Zn_{LC}^{2+}

Coordination number	ΔR [a]/nm	$\Delta\Delta E$ [b]/kcal mol^{-1}
5	0.017	−59.1
4	0.017	−24.8
3	0.002	0.0

[a] ΔR relaxation value corresponds to the distance between the initial optimal position of the precursor Mg_{LC}^{2+} and the one substituted by Zn_{LC}^{2+}.

[b] On substituting a Mg_{3C}^{2+} ion by Zn_{3C}^{2+} the total energy of $Mg_{31}ZnO_{32}$ amounts to −10871.95 eV, which is taken as a reference.

known [14,15] 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 [16] when studying adsorption of a CO molecule on the (0001) polar surface of ZnO. The latter system 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 discussions

3.1. Isomorphic substitution of Mg_{LC}^{2+} by Zn_{LC}^{2+}

Calculated relative energies of substitution of Mg_{LC}^{2+} by Zn_{LC}^{2+} in Zn/MgO cluster model and relaxation of Zn ions are shown in Table 1. It is clear that the substitution of threefold-coordinated Mg_{3C}^{2+} by Zn_{3C}^{2+} is more favourable by energetics than the other two ones.

Under such a substitution the Zn_{LC}^{2+} ion is 'dragged-out' from the optimal position of precursor Mg_{LC}^{2+} ion; the latter results are in good

agreement with available ab initio calculations [17]. For example, the relaxation of a Zn_{5C}^{2+} ion on the (001) surface of Zn/MgO is equal to 0.021 nm according to [17]. Similar results were also obtained for Zn/Li/MgO system. In the latter case the number of molecular clusters corresponds to the zinc-substituted Li/MgO units and it is equal to 9. For simplicity, only 3 clusters are considered, when Li_{LC}^{+} corresponds to Li_{3C}^{+}. The relative energies in this case are equal to 0.0, −26.0 and −71.3 kcal/mol, corresponding to substitution of 3-, 4- and 5-coordinated magnesium ions by Zn^{2+}. It should be noted, however, that such a substitution needs some extra energy. Thus, for example, the substitution of Mg_{3C}^{2+} by Zn_{3C}^{2+} applying the following overall reaction based on our calculations of total energy differences:

$$Mg_{32}O_{32} + Zn(OH)_2 \rightarrow Mg_{31}ZnO_{32} + Mg(OH)_2 \quad (1)$$
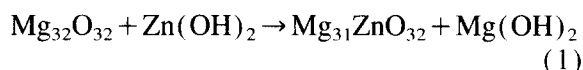
is energetically unfavourable by 17.8 kcal/mol. This might be perhaps the explanation of the conclusions drawn in [8] that no solid solutions of Zn^{2+} in either CaO or $Ca(OH)_2$ are known, and only small amounts of Ca^{2+} cations are exchanged by Zn^{2+} in the near surface region forming the pseudo-solid solution.

3.2. Adsorption and activation of methane

The heterolytic dissociative chemisorption of a methane molecule was examined on various active centres of acid–base pairs. These interactions have been assumed to be responsible for the initial activation of methane under catalytic reaction conditions (800–1100 K) [10]. In the calculations a full optimization of the geometry of the chemisorbed complexes was carried out. In the Zn/Li/MgO molecular cluster the number of potentially possible acid–base pair centres for methane activation is rather high: these may be Li_{LC}^{+}–O_{LC}^{2-}, Zn_{LC}^{2+}–O_{LC}^{2-} as well as Mg_{LC}^{2+}–O_{LC}^{2-} pair centres. Moreover, these numbers are increased by variation of the LC number and by the possibility to form metal–methyl or metal–H bonds. But as was shown in [9,10] some of these com-

Table 2
Dissociative chemisorption energies (ΔE) of methane molecule on some acid–base pairs of active centres of Zn/Li/MgO as calculated by the MINDO/3 method

Pair of centres	Zn	Li	ΔE [a]/kcal mol^{-1}
$Zn^{2+}_{3C}-O^{2-}_{4C}$	Zn^{2+}_{3C}	Li^{+}_{3C}	28.4
$Mg^{2+}_{3C}-O^{2-}_{4C}$	Zn^{2+}_{3C}	Li^{+}_{3C}	-3.0
$Mg^{2+}_{3C}-O^{2-}_{4C}$ [b]	–	Li^{+}_{3C}	9.1
$Zn^{2+}_{3C}-O^{2-}_{4C}$	Zn^{2+}_{3C}	Li^{+}_{4C}	22.3
$Mg^{2+}_{3C}-O^{2-}_{4C}$	Zn^{2+}_{3C}	Li^{+}_{4C}	-10.4
$Zn^{2+}_{4C}-O^{2-}_{3C}$	Zn^{2+}_{4C}	Li^{+}_{3C}	29.4
$Zn^{2+}_{4C}-O^{2-}_{4C}$	Zn^{2+}_{4C}	Li^{+}_{3C}	5.0
$Mg^{2+}_{4C}-O^{2-}_{3C}$ [b]	–	Li^{+}_{3C}	5.0
$Mg^{2+}_{4C}-O^{2-}_{4C}$ [b]	–	Li^{+}_{3C}	-15.1
$Zn^{2+}_{4C}-O^{2-}_{5C}$	Zn^{2+}_{4C}	Li^{+}_{3C}	-6.2
$Zn^{2+}_{4C}-O^{2-}_{3C}$	Zn^{2+}_{4C}	Li^{+}_{4C}	23.2
$Zn^{2+}_{4C}-O^{2-}_{4C}$	Zn^{2+}_{4C}	Li^{+}_{4C}	3.1
$Zn^{2+}_{4C}-O^{2-}_{5C}$	Zn^{2+}_{4C}	Li^{+}_{4C}	-10.6

[a] Positive values correspond to stabilization of chemisorbed methane.

[b] Ref. [10]; the ΔE values correspond to Li/MgO not doped with Zn.

binations may be set aside in view of energetics. Thus, first of all the activation of the methane molecule by $Li^{+}_{LC}-O^{2-}_{LC}$ pair of centres is unfavourable by energetics; the formation of the metal–H bond is less favourable than of the metal–methyl bond [10]. Calculated energies for dissociative chemisorption of a methane molecule on more active acid–base pair centres of Zn/Li/MgO when both Zn^{2+}_{LC} and Li^{+}_{LC} ions corresponding to substitution of 3- or 4-coordinated precursor centres are shown in Table 2. From these data it is clear that activation of the methane molecule via dissociative chemisorption on $Zn^{2+}_{LC}-O^{2-}_{LC}$ pair centres is more favourable by energetics than on the $Mg^{2+}_{LC}-O^{2-}_{LC}$ ones. Moreover, in the case of Zn/ Li/MgO the number of paired active centres which are responsible for initial activation of the methane molecule is higher than both for pure MgO [9] and for lithium-doped Li/MgO [10]. Thus, in the former case of Zn/Li/MgO dissociative chemisorption of the methane molecule can proceed not only via participation of 3-fold coordinated acid–base pair centres but also with participation of 4-fold coordinated $Zn^{2+}_{4C}-O^{2-}_{4C}$ pair centres. Assuming that the activity of the various centres corresponds to the rate of formation of methyl species which lead to C_{2+} hydrocarbons their selectivity should be increased. These results might be considered as an explanation of the experimental observations of increasing C_{2+} selectivity on a NaOH/CaO catalyst modified by zinc cations in the surface. The decrease in selectivity of this catalyst at higher zinc oxide concentrations is probably due to the formation of ZnO clusters on the surface which favour non-selective methane conversion as explained above.

Acknowledgements

References

[1] G.E. Keller and M.M. Bhasin, J. Catal., 73 (1982) 9.
[2] W. Hinsen and M. Baerns, Chem. Ztg., 107 (1983) 223.
[3] J.-L. Dubois and Ch.J. Cameron, Appl. Catal., 67 (1990) 49.
[4] F.S. Stone, E. Garrone and A. Zechina, Mater. Chem. Phys., 13 (1985) 331.
[5] V.D. Sokolovskii, React. Kinet. Catal. Lett., 35 (1987) 337.
[6] T. Ito and J.H. Lunsford, Nature (London) 314 (1985) 721.
[7] J.H. Lunsford, Langmuir, 5 (1989) 12.
[8] T. Grzybek and M. Baerns, Appl. Catal., 118 (1994) L103.
[9] N.U. Zhanpeisov, A.G. Pelmenschikov and G.M. Zhidomirov, Kinet. Catal., 31 (1990) 563 (Translated by Plenum).
[10] G.M. Zhidomirov and N.U. Zhanpeisov, Catal. Today, 13 (1992) 517.
[11] N.U. Zhanpeisov and G.M. Zhidomirov, J. Strukt. Khim., 33 (1992) 151 (Translated by Plenum).
[12] G.M. Zhidomirov, A.G. Pelmenshikov, N.U. Zhanpeisov and A.G. Grebenyuk, Kinet. Catal., 28 (1987) 86 (Translated by Plenum).
[13] N.U. Zhanpeisov, A.G. Pelmenshikov and G.M. Zhidomirov, Kinet. Catal., 32 (1991) 970 (Translated by Plenum).
[14] C. Satoko, M. Tsukada and H. Adachi, J. Phys. Soc. Jpn., 45 (1978) 1333.
[15] M. Tsukada and T. Hoshino, J. Phys. Soc. Jpn., 51 (1982) 2562.
[16] N.U. Zhanpeisov, G.M. Zhidomirov and M. Baerns, J. Strukt. Khim., 35 (1994) 12 (Translated by Plenum).
[17] E.A. Colbourn and W.C. Mackrodt, Surf. Sci., 143 (1984) 391.