

Palladium-oxide sites for facile methane dissociation

A. Trinchero¹, M. Van den Bossche¹, P.A. Carlsson¹, A. Hellman¹, N.M. Martin²,
J. Gustafson², E. Lundgren², and H. Grönbeck^{1*}

¹Competence Centre for Catalysis, Chalmers University of Tech., 41296, Göteborg, Sweden

²Division of Synchrotron Radiation Research, Lund University, Box 118, SE-221 00, Sweden

*corresponding author: ghj@chalmers.se

Introduction

It is generally a challenge to determine the active phase of heterogeneous catalysts during operating conditions. This is valid, in particular, for structurally ill-defined catalysts that are realized as metal particles dispersed on a porous oxide. One example is the active phase of palladium during complete methane (CH₄) oxidation to water and carbon dioxide. This important reaction has recently regained interest because bio- and natural gas are used as fuels in automotive applications. Methane is the main component in such fuels and there is currently a need for catalysts with enhanced low temperature activity. The high activity measured for catalysts based on supported palladium has previously been attributed to different Pd/PdO_x phases [1], such as reduced (metallic) palladium, metal supported surface oxides and bulk metal oxide.

Here, the active phase of Pd during methane oxidation is investigated by density functional theory calculations in combination with in situ high resolution XPS and surface x-ray diffraction measurements. Particularly low activation energies for methane dissociation are measured and calculated for the bulk PdO(101) surface. The calculations reveal that the effect is a ligand effect of under-coordinated palladium atoms in the surface and suggest that single atoms dispersed in oxides with suitable structure could act as sites for efficient methane dissociation.

Materials and Methods

Density functional theory calculations [2,3] are performed to investigate relevant reaction barriers and stability of intermediates for a large set of palladium and palladium oxide surfaces together with Pd guest atoms in oxide matrices. In addition, a first-principles based micro-kinetic model is constructed to calculate turnover frequencies for methane oxidation and coverages of surface species. The methodology enables comparisons between the theory and experiments both for methane conversion into CO₂ and H₂O and the state of the surface as measured by in situ surface x-ray diffraction.

Results and Discussion

The rate determining step (RDS) in CH₄ oxidation is generally assumed to be the removal of the first H atom, whereupon adsorbed CH₃ and H are formed. The present work support this view, and the dissociative adsorption of methane can be used as a measure of the catalytic activity. The results show that a low barrier for methane dissociation is obtained either on under-coordinated Pd-sites in PdO or on metallic Pd, where the lowest barrier is calculated for an under-coordinated Pd site on PdO(101).

The surface oxide on Pd, which consists of a PdO(101) monolayer, is found to have a high barrier for methane dissociation. Instead, two monolayers of PdO(101) have properties

similar to bulk PdO(101) [4,5]. This shows that that the precise coordination of the active Pd atoms in the surface is crucial.

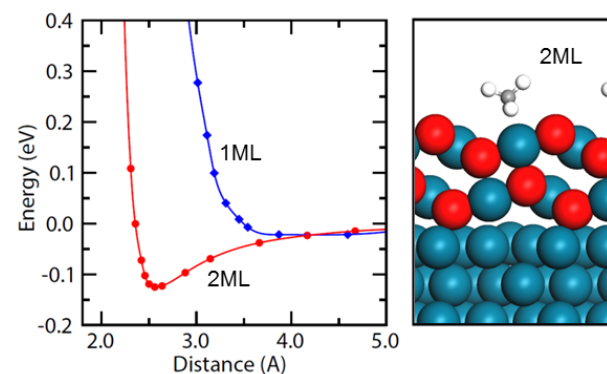


Figure 1 (Left) The potential energy curves for CH₄ approaching 1 and 2 monolayers (ML) of PdO(101) supported on Pd(100). (Right) Structural model for CH₄ adsorbed on 2 ML.

Analysis of the electronic structure of the PdO(101) uncovers that the favorable properties of thick PdO(101) films is related to reduced electrostatic repulsion which enable dissociation close to the final state. The understanding provides a theoretical handle to propose sites with high activity and suggests that it should be possible to design such sites via dispersed late transition metal atoms in oxides that adopt the suitable structure [6]. The calculations are supported by in situ high resolution XPS and surface x-ray diffraction measurements [4,5].

Significance

Sites active for methane dissociation over palladium-oxide has been determined by density functional theory calculations in combination with in situ surface x-ray diffraction [4] and photoelectron spectroscopy [5]. The results can be used to design catalysts with enhanced low temperature activity [6].

References

1. R. Burch, P.K. Loader, F.J. Urbano, *Catalysis Today*, 27, 243 (1996).
2. J.J. Mortensen, L.B. Hansen, K.W. Jacobsen, *Phys. Rev. B*, 71, 035109 (2005).
3. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
4. A. Hellman, A. Resta, N.M. Martin, J. Gustafson, A. Trinchero, P.-A. Carlsson, O. Balmes, R. Felici, R. van Rijn, J. Frenken, J.N. Andersen, E. Lundgren, and H. Grönbeck, *J. Phys. Chem. Lett.* 3, 678 (2012).
5. N.M. Martin, M. Van den Bossche, A. Hellman, H. Grönbeck, C. Hakanoglu, J. Gustafson, S. Blomberg, N. Johanson, Z. Liu, S. Axnanda, J.F. Weaver, E. Lundgren (In manuscript).
6. A. Trinchero, A. Hellman, H. Grönbeck (submitted).