METHANE C-H BOND ACTIVATION ON METAL OXIDE SURFACES: THE NATURE AND ROLE OF METAL-OXYGEN PAIRS IN REACTION MECHANISMS AND ENERGETICS

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Abstract

Activation of methane by transition metal and metal oxide catalysts is crucial for its utilization as a hydrocarbon feedstock to make value added chemicals. Using Density Functional Theory (DFT) based calculations, we report activation/dissociation and reactions of methane on various facets of CuO and NiO. In this contribution, we 1) provide comprehensive insights into the cooperative roles of the under-coordinated surface metal-oxygen pair in methane activation on different facets of these oxides 2) compare and contrast activation mechanisms, the role of lattice oxygen and energetics on different facets of these oxides 3) compare and contrast the metal-oxygen interaction on different facets on these oxides and its effect on reaction mechanisms and energetics. Insights from this investigation may serve as a guideline to screen potential metal oxide surfaces for methane utilization.

Keywords

Methane activation, Transition metal oxides, Density Functional Theory (DFT).

Introduction

Activation of the stable C-H bond of methane is acknowledged to be the most relevant kinetic step in the transition metal/metal-oxide catalyzed reactions of methane (Chin et al., 2013) to make value added chemicals and fuels. Lattice oxygen in metal oxides is known to participate in C-H bond activation (Weaver et al., 2014) and its involvement influences kinetics and thermodynamics of the reactions (Chin et al., 2013). The role of lattice oxygen and the extent of influence in C-H bond activation depends on both geometric and electronic effects originating from the metal-oxygen interaction, surface atomic arrangement and surface coordination (Van Santen et al., 2015). Thus, gaining mechanistic insights into the C-H bond activation of methane on different facets of transition metal oxides and a fundamental understanding of the electronic and geometric effects are crucial for catalyst design for methane utilization.

Using first principles calculations, the activation and reactions of methane on two common and easily synthesized transition metal oxide catalysts, CuO and NiO, are investigated. Distinct mechanisms of methane activation, involving metal and oxygen atoms on different facets of these oxides are investigated, the energetics along these pathways calculated and the intrinsic nature of the oxide surfaces which determine the activation mechanism and energetics are explained.

Computational Methodology

Spin polarized calculations were performed with the periodic plane-wave implementation of Density Functional Theory (DFT) (Kohn and Sham, 1965) using the ab-initio total-energy and molecular dynamics program VASP (Vienna Ab-Initio Simulation Program) developed at the Fakultät für Physik of the Universität Wien (Kresse and Furthmüller, 1996). The GGA-PBE (Perdew et al., 1996) exchange correlation functional and the Projector Augmented Wave (PAW) (Kresse and Joubert, 1999)

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method with a plane wave cut-off energy of 450 eV were used in the calculations. The nudged elastic band (NEB) method was used to locate the transition states (TS) for the dissociation of methane on the different surfaces.

Results and Discussion

CuO was recently shown to be an efficient catalyst in activating the formyl C-H bond in sugars, which is a key step in their oxidation to acids (Amaniampong et al., 2015). Our investigation suggests that CuO is also extremely efficient in activating methane. In contrast, clean Cu surfaces are known to be an inactive for methane dissociation (Xing et al., 2011).

a) Cu(111)- Oxidative addition
Barrier: 169.8 kJ

b) CuO(111)- Concerted oxidative addition & hydrogen abstraction
Barrier: 76.6 kJ

c) CuO(111)- Hydrogen abstraction
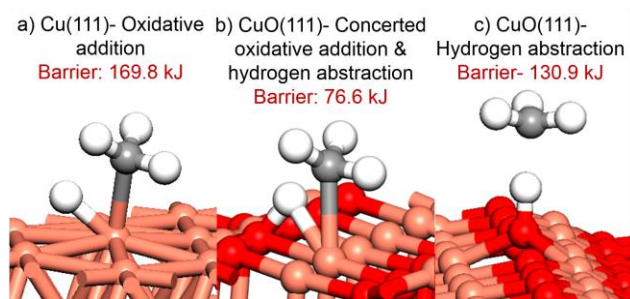Barrier- 130.9 kJ

*Figure 1. Schematic representation of the mechanism of activation of the C-H bond of methane on **a)** Cu(111) surface **b)** CuO(111) surface with synergistic roles of both the copper and lattice oxygen atoms and **c)** CuO(111) surface with involvement of only the lattice oxygen atom.*

Methane activation on the most stable facet, CuO(111), involves a pair of under-coordinated copper and lattice oxygen atoms unlike a Cu surface where it is only a copper atom as shown in Fig.1. The Cu-O pair synergistically activates methane as shown in Fig.1b with the barrier less than half that on clean Cu surfaces. The low barrier of ~77 kJmol^{-1} for dissociation of methane on CuO surfaces can be attributed to the stabilization of the transition state as well as the products of dissociation.

The other mechanism involves only the lattice oxygen as shown in Fig.1c and has much higher barriers. The weaker the binding of the lattice oxygen to the surface, the stronger is its ability to abstract hydrogen from methane in this mechanism Different CuO facets exhibit the following activation efficacy in this mechanism: CuO(110) > CuO($\bar{1}$11) > CuO(111) ≈ CuO(01$\bar{1}$).

The dissociation of methane on the most stable NiO(100) facet also proceeds by the involvement of both the nickel and oxygen atoms. However, the activation barrier for this mechanism is nearly twice that of dissociation on clean Ni surfaces (Xing et al., 2011). This is a contrast compared to the case of Cu and CuO surfaces.

Our simulations suggest that the higher energy facets of NiO, although less stable, are more efficient in activation of methane. The activation barriers for dissociation of methane on these high energy facets of NiO were found to be comparable to that on clean Ni surfaces.

The activation efficacy of the different NiO facets was found to follow the trend NiO(111) > NiO(110) > NiO(100). The strong Ni-O bonding and the differences in surface coordination of the Ni-O pair on the different NiO fects are responsible for the observed trend in methane activation.

Conclusions

Our investigations suggest that both CuO and high energy facets of NiO have great potential in activating methane. Activation proceeds by synergistic catalysis by the under-coordinated M-O pairs on these oxide surfaces. The nature of M-O bonding on the different oxide surfaces is critical in determining the efficacy of activation as it influences the stabilization of the transition state and the products of dissociation. The insights from this investigation provides a guideline to screen potential oxide surfaces for application in methane conversion processes.

Acknowledgement

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