

A FIRST PRINCIPLES ANALYSIS OF METHANOL DEHYDRATION OVER WO_x/ZrO_2

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Summary

First principle density functional theoretical calculations were carried out to examine the likelihood of various proposed mechanisms in the dehydration methanol to dimethyl ether (DME) over different WO_x/ZrO_2 surfaces. This is a characteristic probe reaction for acid sites and also an important in step in the methanol to gasoline process. The activation barriers and mechanisms were examined over different domain size zirconia-supported WO_x clusters models which include monomeric WO_5 clusters, W_2O_9 dimers and WO_3 monolayers. The bridging oxygen atoms in W-O-Zr were found to be the active acid sites for the dehydration. The transition state for methanol dehydration was characterized by the formation of planer carbenium ion which subsequently bonds to a local terminal oxygen site. Our results indicate a second methanol molecule helps to stabilize the positive charge that results on the CH_3 carbenium ion transition state and allows for the simultaneous formation of DME which has a significantly lower barrier than the sequential reaction path. Larger size of WO_x cluster provide more bridging oxygen sites and as such can aid in the delocalization of charge in the transition state thus resulting in lower dehydration energy barriers.

Keywords

Computational Catalysis, Reaction Path Analysis

Introduction

Methanol dehydration to dimethyl ether (DME) is the first step of forming olefins, aliphatics, and aromatics from methanol.^{1,2} Various theoretical studies have been carried out over zeolite cluster models that suggest three plausible pathways and mechanisms for the formation of DME.³ The key factor for each of these involves stabilizing the carbenium ion transition states that form. Recent experimental efforts reveal that specific WO_x/ZrO_2 nanoclusters can be quite active in converting methanol to DME. Little however is known about the active site or the role the influence of cluster size. Herein we examine a series of plausible mechanisms that can control the dehydration of methanol over zirconia-supported tungsten oxide in order to understand the chemistry and to establish structure property relationships which describe the surface chemistry.

Supported tungsten oxide is an active solid acid catalyst for the cracking, isomerization and oligomerization of various hydrocarbon intermediates.^{2,4} The solid acidity of tungsten oxide has been found to be a critical in its catalytic performance. Experimental literature suggests that different tungsten oxide domains supported on ZrO_2 can have marked catalytic activity. Increasing the surface tungsten coverage from isolated surface WO_x to monolayer surface WO_x , leads to the formation of

polytungstate surfaces intermediates that are highly reactive in carrying out isomerization.^{5,6,7}

Methanol dehydration is used herein as probe to investigate the structure-property relationship of supported WO_x/ZrO_2 . The results are compared to previous results on phosphotungstic acid, and literature results on zeolitic surface.^{3,8,9} A series of surfaces with different tungsten oxide domain sizes were modeled to investigate the domain size effect in WO_x/ZrO_2 system. Density functional theory (DFT) calculations were carried out to probe the mechanisms that control methanol dehydration, and the corresponding kinetics.

Computational methods

Periodic density functional theory calculations were carried out using the Vienna ab initio simulation program (VASP) to compute the reaction energies and activation barriers for the elementary steps involved in the methanol dehydration over the WO_x/ZrO_2 surface.¹⁰ The ZrO_2 support was modeled here as the (1 0 0) surface from the bulk optimized cubic zirconia. Non-local gradient corrections to the exchange-correlation potential were done with the Perdew-Wang (PW91) model.¹² Ultrasoft pseudopotentials were employed to describe electron-ion interactions.¹¹ A cutoff energy of 400.0 eV for the plane-

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wave basis set and $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh was employed in all calculations. The ZrO_2 (1 0 0) surface was modeled using a 4×4 super cell with approximately 20 \AA of vacuum space between consecutive z-direction slabs. The bottom two layers were held fixed at the bulk-phase positions while the upper two layers were allowed to relax. Each geometry optimization was optimized to a force of less than 0.05 eV/\AA on each atom. The transition states were described by using nudged elastic band (NEB) method. The force of transition state was optimized to less than 0.10 eV/\AA on each atom.

Results

The results for the dehydration of methanol to DME by sequential and simultaneous additions of methanol are reported in table 1 below.

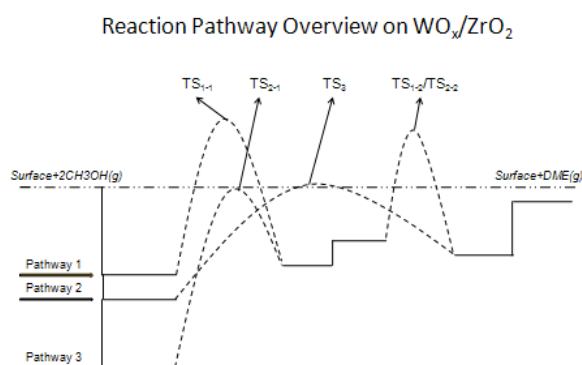


Fig.1 General reaction pathway overview for methanol dehydration on WO_x/ZrO_2 . Path1 and Path2 are sequential reactions with two transition states, and share same second transition state. Path3 are simultaneous reaction with single transition state.

From Figure 1, we can see simultaneous reaction has lower activation barrier than sequential reactions because the second methanol molecule can help stabilize the carbenium ion in transition state. If we have second methanol involved in sequential reactions step 1 (pathway 2), the activation barrier will also be significantly reduced.

Table 1 – Activation barriers on different size of domain

Catalysts	Ea1-1	Ea1(2)-2	Ea2-1	Ea3
WO_5/ZrO_2	1.38eV	1.30eV	1.05eV	1.01eV
$\text{W}_2\text{O}_9/\text{ZrO}_2$	1.31eV	0.97eV	0.93eV	0.96eV
$(\text{WO}_3)_n/\text{ZrO}_2$	1.04eV	0.86eV	0.58eV	0.59eV

Ea1-1, Ea1-2, Ea1(2)-2, and Ea3 are corresponding activation barriers for TS_{1-1} , TS_{1-2} , $\text{TS}_{1(2)-2}$, and TS_3 in Figure. 1.

From Table we see for each elementary reaction, when we increase the domain size of WO_x , the activation barriers will be decreased. The reason for that is large WO_x cluster can provide more bridging oxygen sites, and distribute more charge to stabilize the carbenium ion in transition states. To see that, we compared the positive charge localized in CH_3 of each transition states.

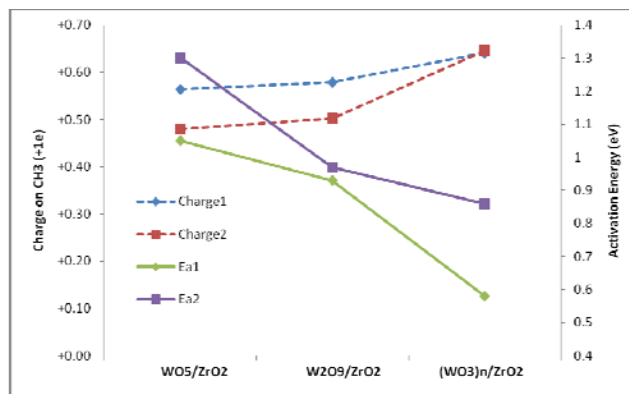


Fig.2 Activation energy and carbenium ion localized charge amount in transition state

Clearly in figure2, the carbenium ion in transition state over larger domain size WO_x/ZrO_2 has more localized positive charge and lower activation energy. That means larger domain size can stabilize more charge in transition state, which will lower the activation barriers.

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