

# Ethanol Oxidation on Metal Oxide Supported Platinum Catalysts

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## Introduction

Ethanol is a renewable fuel that can be used as an additive to gasoline (or its substitute) with the advantage of octane enhancement and reduced carbon monoxide exhaust emissions. However, on the standard three-way catalysts, the conversion of unburned ethanol is low because both ethanol and some of its partially oxidized derivatives are highly resistant to oxidation [1].

To uncover some of the fundamental phenomena associated with ethanol oxidation on Pt containing catalysts, a combination of first-principles density-functional theory (DFT) based calculations and in-situ diffuse reflectance infrared spectroscopy (DRIFTS) analysis was employed. In particular, the objective was to analyze the role of the oxide (i.e.,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>) substrate on the ethanol oxidation activity.

## Materials and Methods

Calculations were performed on 5-layer-thick  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (110) and 4-layer-thick SiO<sub>2</sub> (001) quartz periodic slabs separated by vacuum layers. The adsorbates (metal particles) and the top surface layers were fully relaxed, keeping the bottom layer fixed. The calculations were based on the generalized gradient approximation (GGA) for exchange and correlation, and plane waves. We used ultrasoft scalar relativistic pseudopotentials and the VASP codes. The minimum reaction paths for the decomposition reactions were found using the nudged-elastic-band (NEB) method.

DRIFTS studies were performed on a Magna 750 FTIR system (Nicolet) equipped with a commercial high temperature DRIFTS cell (SpectraTech). Catalyst samples were prepared by the incipient wetness technique. Oxide supports, i.e., aluminum oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 220 m<sup>2</sup>/g) and silicon oxide (SiO<sub>2</sub>, 250 m<sup>2</sup>/g), and dihydrogen hexachloroplatinate (IV) hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 99.9%) were purchased from Alfa Aesar. The amount of noble metal added per gram of dry support was 0.05 millimoles. After impregnation, the samples were dried overnight at 378 K and calcined at 773 K for 2 hours.

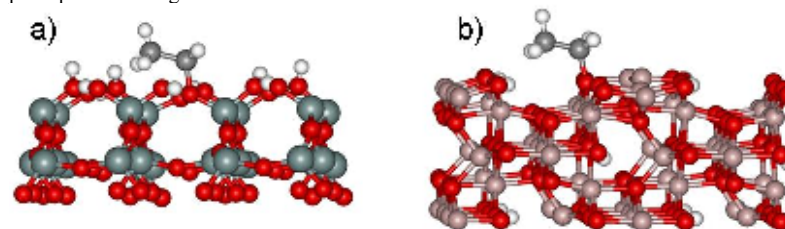
## Results and Discussion

A comparison of the fully hydrogenated SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces shows that all the O-H bonds at the hydrogenated quartz surface are equivalent and strong (~4.5 eV) while at the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, the O-H binding energy depends on the coordination of O atom and may vary in a wide range between 1.2 eV and 3.0 eV [2]. The presence of one OH peak on silica (3747 cm<sup>-1</sup>) and several OHs (3730, 3687 cm<sup>-1</sup>) on alumina is confirmed by the DRIFTS spectra. Such a great difference between the two substrates means that H atoms can be

removed from the alumina surface much easier than from silica (e.g., by oxygen component of the air flow near the surface (the same flow that is employed for the ethanol oxidation)).

The two oxides are also different in anchoring of the intermediates. The most likely scenario for interaction between an ethanol molecule and the hydrogenated oxide surface is the formation of hydrogen bonds, with a subsequent formation of water molecule that leaves the surface, and an attachment of the CH<sub>3</sub>CH<sub>2</sub>- fragment to an oxygen atom at the surface (Fig. 1). The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, however, binds this fragment much weaker (~0.7 – 1.0 eV) than the SiO<sub>2</sub> surface (~4.2 eV). Therefore, alumina surface provides much higher mobility of the fragments of ethanol molecules than the SiO<sub>2</sub> surface because of (i) its weak binding; (ii) a presence of unhydrogenated O sites where the CH<sub>3</sub>CH<sub>2</sub>- radicals can be temporary trapped.

Pt nanoparticles trap and accumulate oxygen at their surface and perimeter sites and play the role of “stoves” that burn ethanol molecules and their partially oxidized derivatives to the “final” products. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces with higher mobility of the CH<sub>3</sub>CH<sub>2</sub>- fragments provides much higher supply rate of these objects to the Pt particles. This will in turn produce a higher conversion rate of unburned ethanol. The rate of the oxidation process is much higher at Pt nanoparticles than at the oxide surface (where the oxidation occurs due to reaction with oxygen gas). The analysis of the DRIFTS spectra agree well with the DFT-based first-principles modeling and simulation.



**Figure 1.** A schematic of the CH<sub>3</sub>CH<sub>2</sub>- intermediates anchored at A) SiO<sub>2</sub> (001) quartz surface, and B) at the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (110C) surface. Si atoms are shown in large grey balls, C in small grey balls, Al in light brown, O in red, H in white.

## Significance

The work reported in this contribution is an attempt to understand how the choice of the oxide substrate affects the rate of the ethanol oxidation on Pt/oxide catalysts. This is an important step towards the rational design at an atomistic level of novel catalysts with enhanced conversion of unburned ethanol and reduced formation of carbonyls such as aldehydes and ketones, which are irritants, toxic air contaminants, and precursors to smog formation.

## References

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2. Rashkeev, S.N., Sohlberg, K.W., Zhuo, S.P., and Pantelides, S.T., *J. Phys. Chem. C*, **111**, 7175 (2007) 7175.