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Chemical transformations of acetone on ZnO powder

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ABSTRACT

Acetone transformations on ZnO powder encompass a number of practical implications for heterogeneous catalysis, and the interest towards this system has fueled a substantial debate over the nature of the adsorbed molecule and its possible self-reactions. This work combines vibrational analysis and computational density functional theory investigation to reconcile some of the disagreements posed by the previous studies spanning wide range of experimental conditions and a variety of ZnO surfaces. The formation of rehybridized and non-rehybridized enolate species following acetone adsorption is analyzed by varying the molecular coverage in computational investigation using cluster models representing ZnO surfaces, and the resulting vibrational spectra are compared with the experimental measurements. In addition, self-aldol-condensation is explored to offer possible surface-catalyzed reaction pathways. Aldol condensation of acetone results in a stable species – enolized diacetone alcohol. Further transformation of this species into mesityl oxide is found to have a very high kinetic barrier.

1. Introduction

Understanding chemical transformations of acetone over metal oxides presents a unique opportunity both from fundamental and from applied perspectives. On one hand, acetone represents an interesting reactant with a potential to form unusual intermediates, including enol [1–7], on these materials, that are in turn used as supports for metallic catalysts [8,9] and even directly as catalysts themselves [10,11] or electrochemical sensors [12–15]. At the same time, acetone conversion is of practical relevance in a wide variety of synthetic methods targeting fine chemicals, such as mesityl oxide, 4-hydroxy-4-methylpentan-2-one, and methyl isobutyl ketone [2].

Although a number of oxide materials can serve as models for investigating acetone adsorption [1,2,4,6,16–19], ZnO presents one of the most interesting cases. ZnO is produced at about 10^5 tons per year [22] for a variety of fields. Its attractive environmental properties [23,24] allow it to be used in large-volume industrial processes. A number of current applications of ZnO include methanol steam reforming [8] and photovoltaics [20,21]. In some of these applications, adsorption on ZnO powder underlies the very essence of the process. Despite some previous studies on single crystal materials, chemistry of acetone on ZnO powder presents quite a few questions that have not been answered.

There have been several studies attempting to address catalytic ability of ZnO with respect to acetone. Most of this work was performed with the reactions of hydrogenation and hydrogen exchange in mind and also focused on explanation of acetone presence as an important reaction intermediate in a number of catalytic processes. Many of these studies are summarized in a paper by Vohs and Barteau [3] who used temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) to demonstrate that the O-terminated polar $(000\bar{1})$ surface of ZnO is not reactive to acetone and that Zn-terminated (0001) polar surface does react with acetone producing CO and CO_2 around 745 K. The mechanism of acetone adsorption was proposed to involve an enolate intermediate, which was consistent with several previous studies of alcohols on ZnO powder [25–28]; however, the explicit proof of this intermediate was not possible by the experimental methods available.

A study of polycrystalline ZnO used FTIR to follow acetone adsorption and hydrogen exchange at catalytic conditions and in the presence of oxygen at elevated temperatures and did suggest the formation of enolate species [28]. The main complications were the lack of control over the possible surface reactive sites and the presence of oxygen and moisture during the experiments. The knowledge of possible acetone polymerization reactions in the liquid phase in the presence of ZnO [29,30] caused a number of studies to consider pressure, acetone exposure, and temperature dependence of surface reaction mechanisms as key factors determining the reactivity of ZnO towards acetone. However, most of

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the work has reported the results of catalytic conversion rather than the insights into the actual surface reaction mechanisms.

To be more specific, the molecular level studies of acetone on ZnO(0001) surface pointed towards the formation of *fully rehybridized* enolate species [3]; however, comparison with ZnO powder sample seemed to suggest that both a rehybridized enolate species [27,28] and an enolate with a fully intact and unreacted C=C double bond [25] are possible for this reaction. The aldol condensation product – mesityl oxide or diacetone alcohol from acetone adsorption was found on several oxides, including TiO_2, MgO, SiO_2, Al_2O_3 [2,4,39]. However, the conversion of acetone to mesityl oxide on ZnO surface has not been demonstrated [3], although ZnO is known to promote aldol condensation of aldehydes and ketones [3,40].

In an effort to understand the chemisorption process of acetone on ZnO powder materials and to resolve a number of discrepancies between catalytic applications and single crystal ultra-high vacuum studies, the research summarized below will take advantage of a combination of infrared spectroscopy and density functional theory computational studies to explain the initial adsorption of acetone and its further conversion upon higher exposures to ZnO powder catalyst. In addition to explaining the pressure gap, this study will also focus on the $(10\bar{1}0)$ non-polar surface, which comprises about 80% of the ZnO powder. This approach will allow for a reconciliation of the previously reported differences in the studies of this useful and abundant material and expand its potential catalytic applications even further.

2. Experimental section

2.1. Experimental techniques and chemical compounds

The experimental setup for FTIR measurements as well as the preparation and characterization of ZnO powder have been described in detail previously [31–33]. Briefly, A Nicolet Magna-IR 560 spectrometer with a liquid nitrogen-cooled external MCT detector was used to collect the IR spectra at 4 cm^{-1} resolution. Infrared experiments were conducted in a custom-designed chamber that allows in-situ FTIR measurements in a transmission mode [31–33]. The entire optical path was purged continuously by water- and CO_2-free air. The base pressure in this chamber is 1×10^{-6} torr. About 30 mg of ZnO powder (99.99% purity, Alfa Aesar) was pressed onto a tungsten mesh under a pressure of 9 tons using a hydraulic press. The sample was then mounted between two tungsten clamps that allow for resistive heating [33,34]. Thermocouple wires were spot-welded directly to the mesh to monitor the temperature. By annealing ZnO powder sample to 950 K under high vacuum (HV) conditions the well-defined surfaces of this material can be formed. According to the previous studies, this procedure minimizes the number of defects and surface impurities and further cleaning or exposure to oxygen does not substantially affect the chemical reactivity of the surfaces produced [32]. The infrared absorbance spectrum was taken after exposing ZnO powder to acetone vapor at room temperature (1 torr for 2 min exposure in all experiments reported below, with higher exposures not leading to any changes in the absorption spectra). The spectrum for the ZnO powder pressed onto a mesh was used as a background. It was recorded at room temperature after ZnO powder annealed to 950 K for 5 min was cooled back to room temperature. For the annealing experiments, the sample was annealed at the temperatures indicated for 10 s following room temperature adsorption with no addition dosage at elevated temperatures and then the spectra were collected at room temperature.

Acetone (Aldrich Chemical Company, Inc. 99+%) was first purified by multiple freeze–pump–thaw cycles and then dosed into the HV chamber via a leak valve. Both mass spectrometry (using Hiden Analytical mass spectrometer in a separate ultra-high vacuum set-up) and *in situ* gas phase IR measurements were performed to confirm the purity of acetone.

2.2. Computational details

Density functional theory (DFT) calculations were performed using Gaussian 09 suite of programs [35] with B3LYP functional. For all the calculations discussed below, LANL2DZ basis set was employed for optimization and 6-311+G(d,p) basis set was used to perform a single point energy calculation as indicated.

$Zn_{12}O_{12}$ and $Zn_{20}O_{20}$ clusters were used to model the $ZnO(10\bar{1}0)$ surface and a $Zn_{13}O_{13}$ cluster was utilized to simulate Zn(0001) and $Zn(000\bar{1})$ surfaces. The atoms representing the bottom three layers in each model were fixed at their bulk positions to avoid unrealistic distortions during the course of energy minimization. The details of constructing these models are discussed in Ref. [32].

To calculate the adsorption energy of the adstructures, ΔE, the energy of the optimized free molecule and the energy of the corresponding unoccupied cluster model were subtracted from the energy of the adstructure. For mesityl oxide adstructures, one water molecule as a product, two acetone molecules and one unoccupied cluster model were used for this procedure, meaning that mesityl oxide (and related) adstructures were considered to be generated exclusively from acetone adsorption. Transition states were determined using the synchronous transit-guided quasi-newton (STQN) method [36,37]. The presence of a single negative eigenvector in these calculations confirms the convergence to a transition state.

Infrared spectra were predicted using B3LYP/LANL2DZ approach followed by a single point calculation with the 6-311+G(d,p) basis set with a scaling factor of 0.965, which proved to provide a very good agreement in the previously reported studies on ZnO [31,32]. Supplemental material section also contains the results of selected calculations using 6-311++G(d,p) basis set to verify the robustness of the basis sets chosen.

3. Results and discussion

3.1. Initial acetone adsorption

To investigate the initial adsorption of acetone on ZnO, it is important to distinguish the common single crystal surfaces that can lead to strong chemical interaction between these two reactants. Since it has been shown that the O-terminated polar surface is unreactive with respect to acetone [3], the starting point should be the comparison of the adsorption process on Zn-terminated (0001) polar surface and on the non-polar $ZnO(10\bar{1}0)$ surface. As the latter comprises about 80% of all surfaces in the powder material, that is the surface investigated in the initial DFT studies outlined in Fig. 1.

A simple cluster model utilized in these studies includes two neighboring surface Zn—O dimers, as shown underneath the corresponding simplified structures in this figure. As expected, the overall exothermic process follows relatively weak adsorption of acetone and ultimately overcomes a moderate barrier to form a stable enolate species. A similar course of reaction could be followed on a ZnO(0001) surface. However, according to this mechanism, a free-standing enolate with non-rehybridized C=C double bond would be formed, which should be easily identified by vibrational spectroscopy. On the other hand, what would