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Partial oxidation of higher olefins on Ag(1 1 1): Conversion of styrene to styrene oxide, benzene, and benzoic acid

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Abstract

Temperature programmed reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS), and reflection absorption infrared spectroscopy (RAIRS) were used to study the partial oxidation of styrene on Ag(1 1 1). Styrene oxide, benzene, and benzoic acid were identified as partially oxidized reaction products. XPS and RAIRS provide evidence for the formation of a styrene-derived surface oxametallacycle that either forms styrene oxide or is further oxidized in a branching reaction to form benzoate, which is the intermediate responsible for the formation of both benzene and benzoic acid. The strong dependence of the product distribution on oxygen coverage suggests that O monomers adsorbed on Ag(1 1 1) provide a higher selectivity for partial oxidation than oxygen from the Ag(1 1 1)–p(4×4)-O reconstruction.

Keywords: Styrene oxidation; Ag(1 1 1); Styrene oxide; Benzene; Benzoic acid

1. Introduction

Ethene oxide is an important chemical intermediate that is produced in large scale by the partial oxidation of ethene over Ag catalysts. This reaction is one of the most important petrochemical processes. Ethene epoxidation has attracted extensive experimental and theoretical research over the last 2–3 decades both to elucidate the basic mechanism and to increase the selectivity of the reaction [1–3].

Experimental studies of ethene epoxidation under ultrahigh vacuum (UHV) conditions have the potential to provide insights into the basic steps involved in the partial oxidation of ethene. However, ethene does not react with co-adsorbed O on Ag under UHV conditions but desorbs before any reaction takes place [4]. Therefore, UHV studies of alkene epoxidation depend on the use of higher molecular weight olefins with desorption activation barriers above the activation barrier for partial oxidation. For instance, norbornene [5], styrene [3,6–8], and 3,3-dimethyl-1-butene [9] have been used to study the partial oxidation of olefins under UHV conditions. These molecules have in common that they do not contain allylic H atoms which are generally believed to be readily abstracted by chemisorbed O atoms on Ag, ultimately preventing partial oxidation processes and leading either to combustion or oxydehydrogenation [2,3,5].

While a general consensus seems to exist on the general mechanism of the partial oxidation of ethene, little is known about the partial oxidation of larger alkenes and the influence of functional groups on reaction products and selectivities. In this paper, we present a detailed study of the partial oxidation of styrene on Ag(1 1 1) under UHV conditions using temperature programmed reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS), and reflection absorption infrared spectroscopy (RAIRS).

Styrene oxidation is widely used as prototypical system for the epoxidation of alkenes in UHV studies. Partial oxidation of styrene to styrene oxide has been observed on Ag(1 0 0) [7], Ag(1 1 1) [6,8], Cu(1 1 0) [10], Cu(1 1 1)

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[11], and recently also on Au(1 1 1) [12]. These studies indicate that styrene oxidation under UHV conditions is a good model for ethene oxidation [3,13]. In steady-state flow reactor experiments, however, styrene was observed to oxidize relatively slowly and no partial oxidation products were found [14].

In contrast to previous observations that styrene oxide is the only partially oxidized reaction product on Ag(1 1 1) [6] and Ag(1 0 0) [7], recent work from our group shows that benzoic acid and benzene are produced from styrene oxidation on Ag(1 1 1) in addition to styrene oxide [8]. This paper presents more detailed results on the partial oxidation mechanism of styrene on Ag(1 1 1). We propose a reaction model based on two different reaction intermediates formed sequentially during TPRS. The model explains all observed reaction products and is consistent with the XPS and RAIRS results. Furthermore, our findings suggests an explanation for the apparent discrepancy between previous UHV studies showing the epoxidation of styrene on Ag [6,7] and the absence of partially oxidized reaction products in higher pressure steady-state experiments [14].

One important issue for understanding the mechanism of epoxidation of olefins is the nature of the reaction intermediates. There are two possible ways for the addition of oxygen to the C=C bond. The O atom can either form bonds to both C atoms simultaneously or sequentially. During the latter mechanism, a surface oxametallacycle may be formed on the surface. Evidence for the sequential addition with the formation of an oxametallacycle intermediate is provided by both theoretical [15–18] and experimental studies [19–22].

In the case of styrene, two distinct oxametallacycle geometries exist. In the linear configuration, the phenyl group is attached to the oxametallacycle C atom that bonds to the surface. In the branched configuration, the phenyl group is attached to the oxametallacycle C that bonds to the O atom. These two geometrically distinct configurations may lead to a branching reaction that limits the selectivity of the partial oxidation of styrene.

Another open issue is the nature of the active oxygen species in the epoxidation of olefins. The majority of the recent publications agree that atomic oxygen and not molecular oxygen species is responsible for olefin epoxidation (for a recent review see [3]). The Ag(1 1 1) surface is the lowest energy Ag surface and is thus considered as the most prevalent surface in Ag epoxidation catalysts. Scanning tunneling microscopy (STM) studies show that atomic oxygen forms two different structures on Ag(1 1 1): dispersed O atoms (monomers) adsorbed on the surface or the Ag(1 1 1)–p(4 × 4)-O reconstruction [23]. This agrees with density functional theory (DFT) results that suggest the existence of O adsorbed at fcc sites at low O coverages while a surface oxide corresponding to the p(4 × 4)-O structure forms at higher coverages [24]. Theoretical calculations also predict that the Ag(1 1 1)–p(4 × 4)-O reconstruction is stable under typical reaction conditions for industrial ethene epoxidation [25]. DFT calculations comparing ethene epoxidation on Ag(1 1 1) with O monomers and on the Ag(1 1 1)–p(4 × 4)-O structure suggest that epoxidation proceeds in both cases through an oxametallacycle intermediate [17]. In this paper, we demonstrate that the reaction product distribution on Ag(1 1 1) depends strongly on the oxygen coverage, providing evidence that O monomers provide a higher selectivity for partial oxidation of styrene than the Ag(1 1 1)–p(4 × 4)-O structure. This finding agrees with recent calculations of the selectivity of ethene epoxidation on the Ag(1 1 1)–p(4 × 4)-O based on DFT and micro-kinetical modeling that predict a very low selectivity for ethene oxide production [26].

2. Experimental considerations

The experiments were done in two ultra-high vacuum (UHV) systems. The majority of the experiments described below were done in the first UHV system equipped with facilities for X-ray photoelectron spectroscopy (XPS), temperature programmed reaction spectroscopy (TPRS), and low-energy electron diffraction (LEED). The second UHV system combines TPRS and LEED with reflection absorption infrared spectroscopy (RAIRS). We used TPRS and LEED to ensure the reproducibility of the experimental conditions between the two different systems.

The (1 1 1) oriented silver single crystal was cleaned with repeated cycles of Ar ion sputtering followed by annealing to 950 K for several minutes. We used two different (1 1 1)-oriented Ag crystals to test the reproducibility of our results. XPS spectra were acquired with a hemispherical energy analyzer using Mg Kα X-rays as the excitation source. All XPS binding energies are referenced to the $\mathrm{Ag}\,3d_{5/2}$ peak at 367.9 eV. For TPRS measurements the sample was moved close to the ionizer of the quadrupole mass spectrometer (QMS). A small aperture between the sample and the QMS was used to ensure that the QMS detects only molecules that originate from the sample substrate. The sample was heated radiatively by a W filament mounted behind the sample. The heating rate varied from about 8 K/s at 150 K to about 6 K/s at 600 K and was highly reproducible in all TPRS experiments. A negative bias voltage was applied to the sample to repel stray electrons that may cause electron stimulated reactions. A Fourier transform infrared spectrometer with mercury cadmium telluride (MCT) detector was used to acquire the RAIRS spectra with a resolution of $4\,\mathrm{cm}^{-1}$. All coverages and reaction product yields for experiments on the Ag(1 1 1) surface are given in units of monolayers (ML) where 1 ML is equal to 1.5×10^{15} molecules cm^{-2}.

The purity of NO_2, styrene, styrene oxide, and benzoic acid was checked by mass spectrometry. NO_2 (purity 99.5%) was dosed through a 5 mm diameter tube directed at the sample which was positioned about 20 mm from the end of the tube. NO_2 doses given below refer to the background pressure and do not take the enhancement of the direct doser into account. Styrene (purity 99.5%) and styrene oxide (purity 98%) were purified by repeated