The role of water in propylene partial oxidation: thermal desorption studies on Ag(110)

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The desorption and reactions of propylene and propylene oxide adsorbed on atomic oxygen covered and hydroxyl covered Ag(110) were investigated to elucidate the effect of water on the oxidation of propylene over silver catalysts. Previous studies clearly indicate enhancement of propylene partial oxidation by the addition of water to reactor feed streams. Propylene combustion by oxygen adatoms on Ag(110) is completely passivated by water coadsorption on the oxygen atom covered surface (water adsorption on O–Ag(110) results in hydroxyl groups). The desorption activation energy of propylene and propylene oxide is increased by up to 30% by adsorbed oxygen atoms on Ag(110). The desorption activation energy for propylene and propylene oxide is reduced on the hydroxyl covered surface relative to desorption from atomic oxygen covered Ag(110). These results suggest that the inhibition of deep oxidation plays an important role in the previously observed water enhancement. In addition, the decreased desorption activation energies for both propylene, the reactant, and propylene oxide, the desired product, may influence the selectivity of this complex reaction system. Potential changes in catalytic reactivity and selectivity caused by water addition are discussed in terms of a general catalytic reaction rate law.

Keywords: propylene, propylene oxide, oxygen, partial oxidation, hydroxyl groups, water, Ag(110), coadsorption

1. Introduction

The partial oxidation of propylene to propylene oxide is a several billion dollar industry worldwide. Currently, no industrial method for propylene oxide production by direct oxidation of propylene using molecular oxygen is practiced. Silver is a unique material for the partial oxidation of ethylene, and ethylene oxide production is accomplished industrially over promoted supported silver catalysts with selectivities in excess of 80% [1]. Unfortunately, very low selectivity (less than 6%) is generally observed for propylene partial oxidation over silver ethylene epoxidation catalysts [2]. The low selectivity for propylene oxidation compared to ethylene is thought to be related to the lower bond dissociation energies of the methyl hydrogens of propylene which leads to facile hydrogen abstraction and propylene combustion. The catalytic partial oxidation selectivity of propylene to propylene oxide over silver catalysts can be enhanced by up to a factor of 3 by the addition of water to the reactant feed gas as demonstrated by several patents [3,4]. Here we report on a surface science study of the effect of water on the surface interactions of propylene and propylene oxide with oxygen atom modified Ag(110).

A number of studies have been published on the interaction of oxygen and other coadsorbates on silver surfaces in relation to partial oxidation [5–10]. Ag(110) is the most active low index silver surface for oxygen adsorption, and studies related to partial oxidation have predominately been on the (110) surface, although Ag(111) has also been studied in some detail. Oxygen interacts quite strongly with Ag(110) with a desorption activation energy near 42 kcal/mol, however, the dissociative sticking probability is low, $\sim 10^{-4}$ [11]. Most recently, it has been demonstrated that oxygen adsorption at room temperature reconstructs Ag(110) into an added row surface of –Ag–O–Ag–O– chains perpendicular to the rows of silver atoms on the (110) surface [12]. However, oxygen adsorption near 170–190 K does not result in long range order or long chain formation on the surface. Growth of short oxygen–silver chains into the long chains upon sample heating has been shown to reduce the activity of the adsorbed oxygen atoms for the oxidation of CO [13] and propylene [14].

Adsorption of propylene and propylene oxide on oxygen covered Ag(110) has been characterized. Deep oxidation of propylene has been previously observed with no propylene partial oxidation products desorbing [14,15]. In addition to the propylene oxidation, adsorbed oxygen atoms increase the desorption activation energy of coadsorbed unreacted propylene by up to 30% [14]. A similar increase in the propylene oxide desorption activation energy is seen for adsorption on O–Ag(110) but no reaction (further oxidation or isomerization) of the coadsorbed propylene oxide occurs [16]. Similarly, enhanced adsorption of ethylene and ethylene oxide by coadsorbed oxygen has been reported [17,18]. The

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increase in desorption activation energy of propylene and propylene oxide as well as ethylene and ethylene oxide in the presence of oxygen atoms is attributed to the creation of partial positive charge sites on the silver surface by coadsorbed oxygen [14–19]. Water coadsorption has also been studied on oxygen modified Ag(110) [20–22]. Coadsorbed water on oxygen modified Ag(110) results in the formation of surface hydroxyl groups by the reaction of water molecules with adsorbed oxygen atoms. Several states of adsorbed molecular water have been identified on top of the hydroxyl surface. The adsorbed water molecules desorb below 250 K leaving hydroxyl groups which disproportionate at 325 K, forming gas phase water and surface oxygen atoms. Coadsorbed water results in the formation of surface hydroxyl groups at temperatures as low as 80 K [20]. In this letter, the effects of coadsorbed water, resulting in hydroxyl groups, on the reactions and interactions of propylene and propylene oxide with oxygen modified Ag(110) are presented. These results are then related to the enhancement of propylene partial oxidation by water, utilizing a standard form of a catalytic rate law.

2. Experimental

The experimental apparatus used in these experiments was a stainless steel UHV system described elsewhere [23]. The base pressure in the UHV system was typically in the low 10^{-10} Torr range after system bakeout. The Ag(110) sample (Metal Crystals and Oxides) was mounted to a liquid nitrogen cooled sample manipulator by tantalum support wires which allowed for resistive heating of the sample and cooling to ca. 100 K. All adsorbate exposures were accomplished using variable leak valves connected to stainless steel directional dosing arrays. The water and propylene oxide were stored in glass vials connected to the gas dosing manifold. The vapor in the gas manifolds for propylene oxide and water was flushed prior to each exposure to ensure highest purity. During thermal desorption, multiple masses (up to 12) were monitored allowing the desorption spectra of the reactants and products to be monitored.

The hydroxyl covered Ag(110) surface was generated by adsorption of water at 120 K on atomic oxygen precovered Ag(110). The sample was then heated to 210–250 K to remove any adsorbed molecular water from the surface [20]. Organic exposure was performed after the sample had cooled to ca. 100 K. The heating rate during TPD was 3 K/s for all the data presented.

3. Results and discussion

Previous studies of the coadsorption of propylene and oxygen on Ag(110) demonstrate that under vacuum conditions the only reaction products observed are combustion products, H_2O, CO_2 and C_{ads} [14,15]. The extent of the combustion reaction and combustion product distribution is a function of the order/disorder of the surface oxygen atoms and of the surface oxygen/propylene ratio [14]. No propylene partial oxidation products desorb from Ag(110) during TPD experiments. During propylene combustion, carbon dioxide evolution is typically observed in the 400–550 K range and much of the preadsorbed oxygen is consumed. Any unreacted oxygen desorbs at 580 K. In contrast, when propylene is coadsorbed with water on the O–Ag(110) surface, no propylene combustion is observed during thermal desorption. Carbon dioxide formation and oxygen consumption are shown in figure 1 for propylene oxidation with and without coadsorbed water. The same oxygen atom precoverage was employed in both experiments. Figure 1a shows that the reaction of propylene with adsorbed oxygen atoms results in carbon dioxide desorption at 450 K; however, no carbon dioxide desorption is observed when a propylene and hydroxyl covered surface is heated. Similarly, the oxygen TPD (figure 1b) shows that for the same oxygen atom pre-coverage, all the preadsorbed oxygen desorbs when water is coadsorbed and substantial oxygen is consumed in the absence of coadsorbed water. A reference spectrum for oxygen adsorption/desorption from Ag(110) is shown in figure 1b for comparison. Figure 1 demonstrates that the reaction of adsorbed oxygen atoms with water (resulting in surface hydroxyl groups) passivates the oxygen atoms for propylene combustion on Ag(110). The passivation by coadsorbed water of the adsorbed oxygen atoms for propylene combustion may play a significant role in the enhanced selectivity of propylene partial oxidation by the addition of water.

In addition to passivation of the adsorbed oxygen by water, coadsorbed water also lowers the desorption activation energy for propylene. Figure 2 shows the desorption of similar propylene coverages from a clean Ag(110) surface, and from surfaces modified by hydroxyl groups and oxygen atoms. The hydroxyl covered surface was generated using the same protocol as described earlier. Previously, a linear increase in propylene desorption temperature with oxygen atom coverage on Ag(110) has been reported in addition to propylene combustion [14,15]. Here we demonstrate that the increase in binding energy is partially counteracted by water coadsorption. From clean Ag(110), sub monolayer propylene desorption occurs at 177 K with an activation energy of 10.7 kcal/mol and from the 0.3 ML oxygen atom covered surface, desorption occurs at 205 K with an activation energy of 12.5 kcal/mol. When propylene is coadsorbed with water on O–Ag(110), desorption occurs at 193 K with an apparent activation energy of 11.8 kcal/mol. In addition to the effect of water on propylene desorption, water's effect on the desorption of propylene oxide may also play an important role in the catalytic selectivity enhancement.

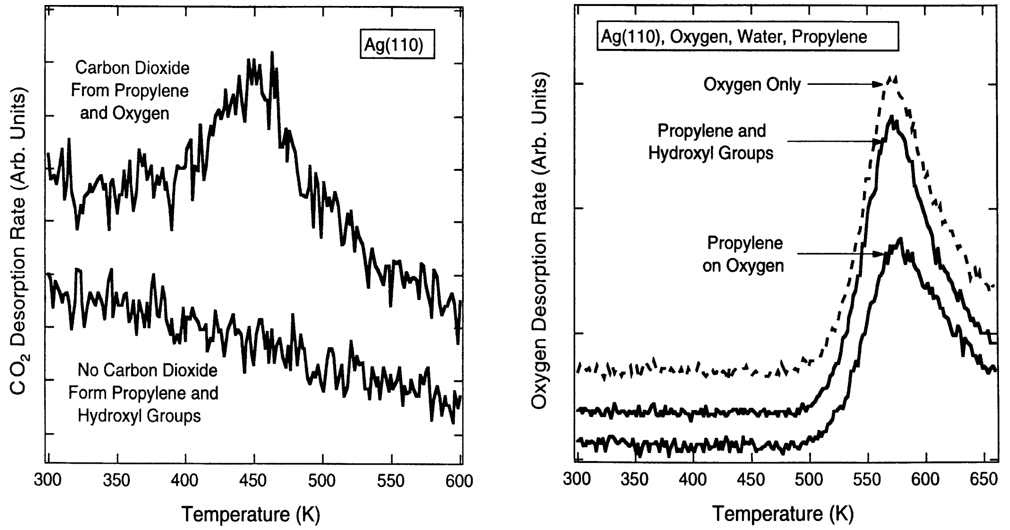

Figure 1. Thermal desorption spectra of carbon dioxide and oxygen from the adsorption of propylene on oxygen covered Ag(110) with and without water coadsorption. The desorption spectra are offset for clarity. Evidence for the passivation of adsorbed oxygen for propylene combustion is provided by the lack of oxygen consumption and lack of carbon dioxide production with coadsorbed water.

The desorption activation energy of propylene oxide (the desired partial oxidation product) from oxygen modified Ag(110) is reduced by water coadsorption, similar to that observed for propylene desorption. No reaction of propylene oxide with adsorbed oxygen atoms has been reported on Ag(110). However, Bare [16] demonstrated an increase in propylene oxide desorption temperature with oxygen coverage. Water coadsorption partially counteracts the observed increase in the propylene desorption activation energy induced by oxygen adatoms. Figure 3 demonstrates the trend in desorption temperature for propylene oxide desorption from clean Ag(110), OH–Ag(110) and O–Ag(110). The initial oxygen atom coverage was 0.3 ML, the same as shown in figure 2 for propylene desorption. These coverages result in propylene oxide desorption from the clean Ag(110), OH–Ag(110) and O–Ag(110) covered surface at 178,

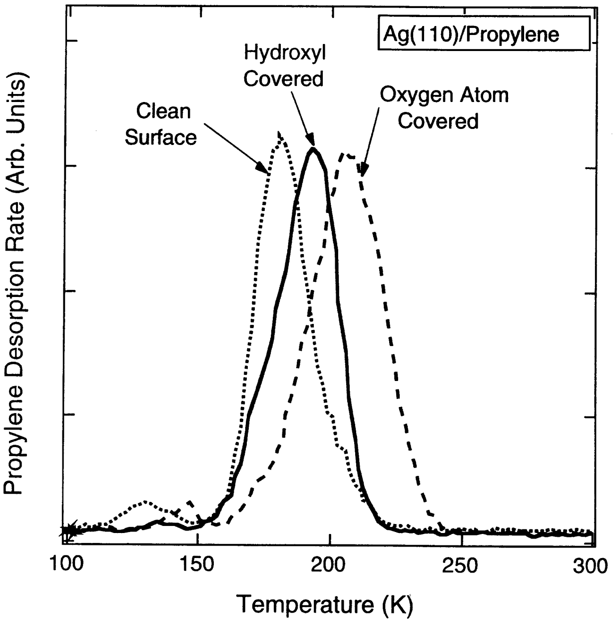

Figure 2. Desorption spectra of propylene from oxygen modified and hydroxyl covered Ag(110) surfaces. The hydroxyl covered surface was formed by water adsorption on the O–Ag(110) and heating to 250 K to remove excess adsorbed molecular water. Note the decrease in desorption temperature (and activation energy) on the hydroxyl covered surface compared to the oxygen covered surface.

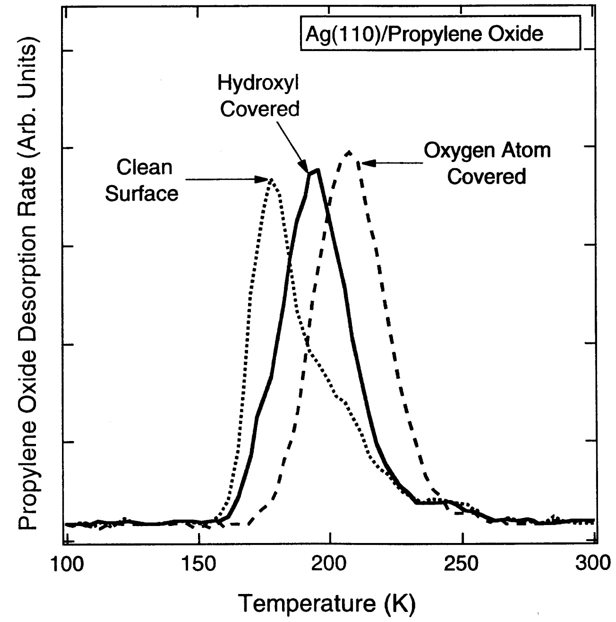

Figure 3. Propylene oxide desorption from oxygen modified and hydroxyl group covered Ag(110). A decrease in propylene oxide desorption temperature (and desorption activation energy) is observed with the coadsorption of water, the decrease in desorption temperature is similar to the decrease for propylene desorption.

195 and 208 K and apparent first order activation energies of 10.8, 11.9 and 12.7 kcal/mol, respectively. By lowering the desorption activation energy of the desired product, one would anticipate the increase in partial oxidation selectivity observed for the addition of water to the propylene/oxygen feed.

The patent literature demonstrates that water enhances the selectivity for propylene partial oxidation to propylene oxide over silver based catalysts [3,4]. However, surface science studies under UHV conditions of coadsorbed oxygen and propylene result only in combustion and no partial oxidation is observed [14,15]. Although no partial oxidation of propylene has been observed on Ag(110), the partial oxidation of norbornene is reported demonstrating that oxygen adatoms on Ag(110) can be active for epoxidation [24]. Therefore, discussion of the partial oxidation reaction is justified in terms of our results even though we do not directly probe this reaction on Ag(110). In the following paragraphs we discuss the results reported here in the context of propylene oxidation reactions under catalytic conditions. The implication of the coadsorbed water results on the high pressure partial oxidation catalysis of propylene can be examined by assuming a Langmuir–Hinshelwood Haugen Watson (LHHW) rate law typical of heterogeneous catalysis [25]. A general form of the LHHW type catalytic rate law is:

$$\text{rate} = (\text{kinetic factor})(\text{driving force})/(\text{surface adsorption group})^{n}.$$

Although complete mechanistic information is not available for this reaction system, based on this qualitative rate law and our current understanding of the competing deep and partial oxidation processes, we rationalize the potential implications of the new results reported here. From this discussion we demonstrate that the TPD results are consistent with selectivity results reported in the patent literature. We start by considering model partial oxidation and combustion reaction rate laws. To simplify the model rate laws, we make the reasonable assumptions that combustion is irreversible. Regardless of the rate limiting steps, rate laws for combustion and partial oxidation should have the form of:

$$\text{rate}_{(\text{combustion})} = k'C(\text{propylene})^{\omega}C(\text{oxygen})^{\sigma}\Big/\left[1+\sum KC\right]^{\alpha}$$

and

$$\text{rate}_{(\text{partial ox.})} = \left[kC(\text{propylene})^{\beta}C(\text{oxygen})^{\gamma} - k''C(\text{propylene oxide})\right]\Big/\left[1+\sum KC\right]^{\alpha'}$$

where the C's represent gas phase concentrations. The numerator gives a lumped rate constant and a driving force in terms of the gas phase concentration of the reactants. The denominator in each of these rate laws represents the adsorption of reactants, products and poisons on the sites involved in the reactions. From the UHV desorption studies of water, propylene and propylene oxide on Ag(110), we know that these species will adsorb reversibly at typical reactor temperatures.

First we examine the blocking of propylene combustion by coadsorbed water, the direct effect of water on the combustion reaction. Under the controlled conditions studied here, water is eliminating sites active for combustion on Ag(110). Coadsorbed water may be occupying the sites active for deep oxidation in a catalytic reactor, in effect, acting like a reversible poison. The addition of water to the feed slows the deep oxidation process, increasing the reaction selectivity. Water is likely passivating the adsorbed oxygen atoms for propylene combustion, as we demonstrate on Ag(110). In terms of the rate law, the denominator of the combustion reaction would increase since the $K^{H_2O}C(H_2O)$ is increased by addition of water, effectively reducing the combustion rate. This is the most direct water effect and likely has the strongest influence on the reaction selectivity of the effects we discuss. A similar effect may be expected on the partial oxidation reaction. However, this effect would not lead to the enhanced selectivity reported [3,4].

Coadsorbed water also reduces the desorption activation energy of the reactant and product (propylene and propylene oxide) on the surface implying that the surface concentration of both species will be lower during steady state catalysis. If the propylene oxide concentration on the surface is lower, the rate of reaction, or turnover, of the active partial oxidation site will increase. In terms of the rate law, the equilibrium constant for propylene oxide is changed, therefore the denominator decreases, increasing the rates. The driving force for partial oxidation is also increased by a reduced surface concentration. If the surface reaction for propylene oxide formation is reversible, a lower desorption activation energy would lower the rate of the reverse reaction. We consider the effect of water on both combustion and partial oxidation even though Ag(110) has not been shown to be active for propylene epoxidation since previous studies demonstrate activity for partial oxidation of other alkenes by oxygen atoms on Ag(110) [24] and Ag(111) [26]. Additionally, if secondary combustion of the desired product occurs, a lower desorption activation energy will lower the secondary combustion reaction rate. However, previous studies indicate that secondary combustion of propylene oxide is not significant over silver catalysts [27].

The lower concentration of propylene on the surface is difficult to relate to an increase in the reaction selectivity. Lower surface concentrations of propylene would result in both slower deep oxidation, and partial oxidation reaction rates by reducing the driving force. However, if the sites for combustion are more strongly affected by water than the partial oxidation sites, this effect would selectively lower the deep oxidation reaction rate by lowering the surface concentration at sites active for combustion. This may be the case since we have clearly identified that adsorbed water can passivate oxygen atoms that are active for combustion. Additionally, if the propylene reaction orders for deep and partial oxidation differ, the reduced desorption activation energy would affect the two rates differently. Clearly the TPD results are consistent with the patent literature and the effects of water on the desorption and reaction of propylene and propylene oxide on oxygen atom modified Ag(110) can be used to rationalize the water enhanced selectivity observed for the catalytic oxidation of propylene.

4. Conclusions

The adsorption of propylene and propylene oxide with and without water on oxygen atom modified Ag(110) have been compared to elucidate the role of water in the partial oxidation of propylene over silver catalysts. Under vacuum conditions, adsorbed oxygen increases the desorption activation energy for both propylene and propylene oxide and results in deep oxidation of adsorbed propylene. When water is coadsorbed on the oxygen modified surface, resulting in hydroxyl group formation, the combustion of adsorbed propylene ceases and the desorption activation energy of both propylene and propylene oxide is reduced relative to desorption from the oxygen atom covered surface.

The thermal desorption studies have been related to propylene partial oxidation over silver catalysts. The reported water enhancement of propylene oxidation selectivity is consistent with these observations. First, water passivates sites active for propylene deep oxidation on Ag(110), possibly increasing the selectivity by blocking of combustion sites occupied with water/hydroxyl on the catalyst surface. Additionally water decreases the desorption activation energy for propylene and propylene oxide which would lead to lower concentrations on the catalyst surface under steady state operations. For propylene oxide the net result of a lower surface concentration would be an increase in the turnover of sites active for propylene oxide production and/or a reduction in the rate of secondary propylene oxide combustion. A lower concentration of propylene on the surface could enhance the selectivity if the lower concentration is primarily realized at deep oxidation sites.

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