# Propene oxidation on Ag(111): spectroscopic evidence of facile abstraction of methyl hydrogen

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Reactions of propene on an oxygen-modified Ag(111) surface were investigated by means of temperature-programmed reaction spectra and reflection–adsorption infrared spectroscopy (RAIRS) at 100 K. In the presence of oxygen adatoms, interactions of propene with the substrate are strengthened. The reaction between propene and oxygen adatoms (0.086 monolayer) produces not only total oxidation products ($CO_2$ and $H_2O$), but also partial oxidation products (CO and acetone). The formation of chemisorbed hydroxyl groups is identified by RAIRS when coadsorbed propene and oxygen adatoms are annealed to 200 K. The formation of hydroxyl is ascribed to the abstraction of methyl hydrogen by oxygen adatoms.

**KEY WORDS:** propene oxidation; Ag(111); RAIRS; TPRS.

## 1. Introduction

Silver-based catalysts, currently used for industrial epoxidation of ethylene, are quite selective, although the detailed mechanism is still a subject of debate [1]. In contrast, propene is epoxidized with very low selectivity from 2% to 4% [2,3]. On Ag(110), experimental and theoretical studies have proposed that the low epoxidation selectivity is due to facile abstraction of methyl hydrogens of propene, a process that facilitates the production of $CO_2$ and $H_2O$ [4–8]. Indirectly favoring this proposal, ultrahigh vacuum (UHV) studies of olefins without a labile allylic hydrogen, *e.g.*, styrene, 3,3-dimethylbutene and norbornene, show good epoxidation selectivity [9–11]. However, no direct experimental evidence has emerged.

Although the close-packed Ag(111) surface is the predominant crystal face present in supported Ag catalysts [12] and powders [13], its inertness to $O_2$ chemisorption under UHV has made it unattractive for surface science studies of oxidation reactions. In this paper we use $NO_2$ as a source of chemisorbed atomic oxygen and, for Ag(111), present the first report of its interactions with propene. Temperature-programmed reaction spectra (TPRS) and reflection–adsorption infrared spectroscopy (RAIRS) were used. Our results reveal interactions between propene and oxygen adatoms that differ significantly from those on Ag(110).

## 2. Experimental

The experiments were performed in a two-level UHV chamber equipped with RAIRS, TPD and AES [14]. The base pressure was $2.0 \times 10^{-10}$ torr. Verified by AES, the Ag(111) surface was cleaned by repeated cycles of Ar sputtering at room temperature followed by annealing to 780 K.

Temperature-programmed reaction experiments were conducted at a ramp rate of $2\,K\,s^{-1}$ and eight signals, accounting for propene ($m/e = 41$), carbon dioxide ($m/e = 44$), water ($m/e = 18$), carbon monoxide ($m/e = 28$), oxygen ($m/e = 32$), acetone ($m/e = 43$), acrolein ($m/e = 56$), and epoxypropane ($m/e = 58$), were monitored simultaneously. Using a mercury–cadmium telluride (MCT) detector, RAIRS spectra were collected by co-adding 1500 scans at $4\,cm^{-1}$ resolution. RAIRS for clean and oxygen-modified Ag(111) were used as references for spectra of propene adsorbed on clean and oxygen-modified Ag(111), respectively.

Due to the extremely low dissociative sticking coefficient of $O_2$ on Ag(111) [15], $NO_2$ was used as the oxygen-atom source. In this method, $NO_2$ is dosed at 508 K to form adsorbed O and gas-phase NO, a process saturating at 0.5 monolayer (ML) of atomic oxygen [16]. Following $NO_2$ decomposition, the sample was evacuated and cooled to 100 K before propene was dosed.

## 3. Results and discussion

Temperature-programmed reaction spectra were recorded after 0.25 L ($1\,L = 1.33 \times 10^{-6}\,Pa\,s^{-1}$) propene

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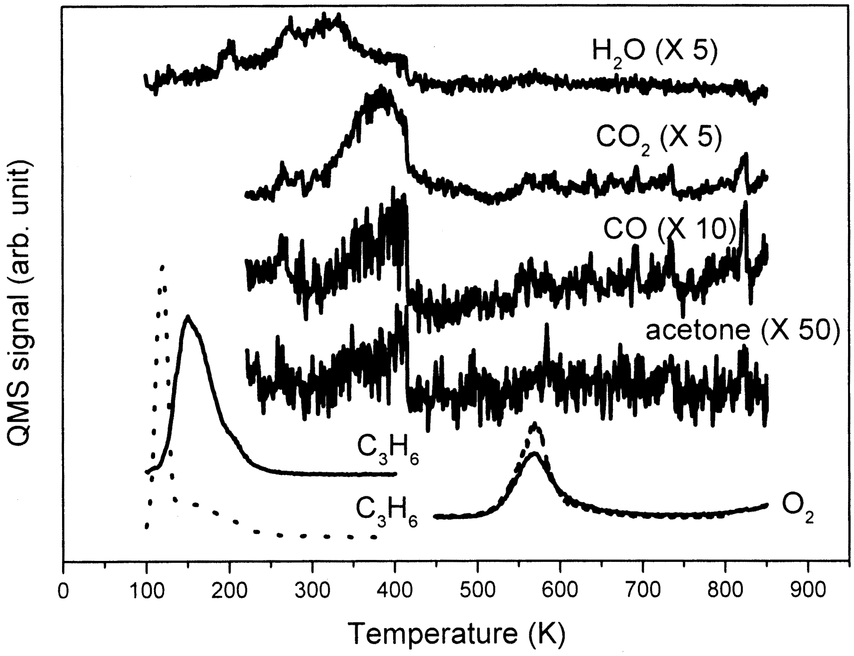

Figure 1. Temperature-programmed reaction spectra taken after 0.25 L propene exposure on oxygen-covered (0.086 ML) Ag(111) at 100 K. The dotted lines are TPD spectra for 0.25 L propene and 0.086 ML oxygen from clean Ag(111), respectively.

was dosed at 100 K on 0.086 ML of atomic oxygen (figure 1). Two reference spectra (dashed lines) are shown for comparison—TPD of 0.25 L propene and TPD of 0.086 ML atomic oxygen.

In the absence of oxygen, propene desorbs with a sharp peak at 123 K accompanied by a broad shoulder at 150 K, corresponding to the desorption of physisorbed and chemisorbed propene, respectively [17]. In the presence of 0.086 ML of oxygen adatoms, a 0.25 L propene dose leads to a broad propene TPD peak centered at 150 K, a peak attributed to chemisorbed propene. The stabilization is attributed to the presence of electron-deficient Ag atoms formed when electronegative oxygen chemisorbs and removes electron density from Ag [18]. As a result, the donation of propene $\pi$ electron density increases, *i.e.*, stabilization [6].

Compared to Ag(110) where only total oxidation products are found [6–8], reactions of chemisorbed propene and oxygen on Ag(111) lead to partial oxidation products and to residual atomic oxygen that desorbs as $O_2$ at relatively high temperatures (figure 1). The partial oxidation products, CO and $CH_3COCH_3$, follow the same TPD profile; we infer that they form *via* the same reaction mechanism. Unlike Ag(110), $O_2$ also desorbs and the signal is strong; comparing the two $O_2$ peaks in figure 1, only 16% of the initial atomic oxygen is consumed to form propene oxidation products. We conclude that, compared to Ag(110), the more densely packed Ag(111) exhibits lower total reactivity but higher partial oxidation selectivity.

Turning to vibrational spectroscopy, figure 2 shows a series of RAIRS spectra following 0.25 L propene doses at 100 K on clean and 0.086 ML O-covered Ag(111). Since the RAIRS for 0.086 ML O-covered Ag(111) was used as reference spectra for propene adsorption on oxygen-modified Ag(111), the positive vibrational peaks at *ca.* 975 $cm^{-1}$ corresponding to surface Ag=O vibration appear in figures 2(b–d). The vibrational assignments are presented in table 1. In the absence of oxygen (bottom curve, labeled a), the spectrum is typical of physisorbed propene. That the C=C stretching mode at 1618 $cm^{-1}$ is observable implies that the ensemble average orientation of the molecular plane of propene is not parallel to the Ag(111) surface [17].

The vibrational spectrum is quite different when 0.25 L propene is dosed at 100 K in the presence of 0.086 ML of atomic oxygen (curve 2b). Based on previous work [17], this spectrum is assigned to chemisorbed propene held in multiple forms, based on four resolved $=CH_2$ wagging modes between 913 and 947 $cm^{-1}$. Perpendicular dipole moment components, induced by interactions of the C=C moiety with the surface, account for the C=C stretching modes at 1610 and 1604 $cm^{-1}$, measurably lower than in the absence of atomic oxygen. Furthermore, increasing the coverage of atomic oxygen shifts these bands to even lower energies. We take this as evidence, consistent with TPD, that oxygen adatoms strengthen the interactions of propene with Ag(111).

When the surface giving curve (b) is annealed to 200 K for 2 min (curve c), there is no longer evidence for C=C stretching, but there is at high energy a new relatively broad and intense peak, centered at 3567 $cm^{-1}$. The absence of C=C is consistent with the desorption of propene (figure 1). Since hydroxyl groups on metals exhibit vibrational transitions between 3500 and 3600 $cm^{-1}$,

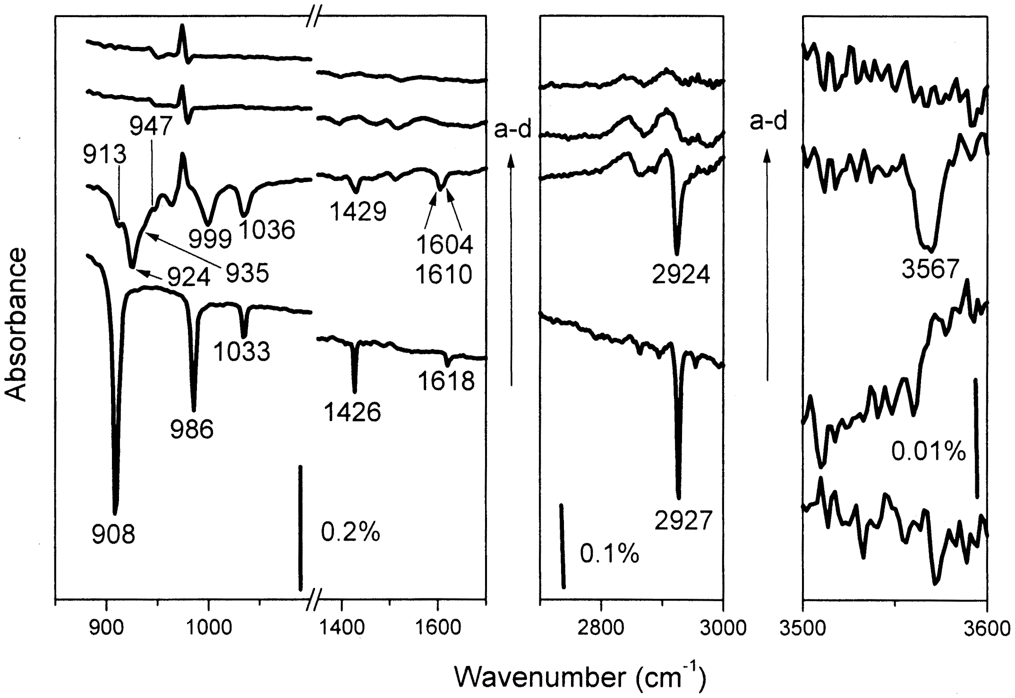

Figure 2. RAIRS spectra of 0.25 L propene doses on (a–d, bottom to top): (a) clean Ag(111) at 100 K; (b) 0.086 ML oxygen-covered Ag(111) at 100 K; (c) same as (b) but annealed at 200 K for 2 min; (d) same as (b) but annealed at 300 K for 2 min. All spectra were recorded at 100 K.

we attribute the strong band at 3567 cm$^{-1}$ to OH formed by partial dehydrogenation of propene in the presence of atomic oxygen.

Regarding its origin, we note that extensive studies of organic reactions with atomically adsorbed oxygen atoms on Ag(110) have established that reaction pathways can be successfully predicted based on the gas-phase acidity of the organic reactant [19]. For propene, the allylic hydrogen is most acidic because the conjugate base (allylic anion) is stabilized through resonance [20]. For example, on Ag(110), propene reacts with atomic oxygen through its acidic allylic C–H bonds, leading to complete combustion [7]. Thus, we attribute the hydroxyl signal to a reaction between oxygen adatoms and the methyl hydrogen of chemisorbed propene that occurs at some point during annealing to 200 K.

The band attributed to OH disappears after annealing at 300 K for 2 min (curve d), a fact consistent with TPD of water between 250 and 380 K (figure 1). We suppose water is formed by disproportionation of hydroxyls. The formation of hydroxyl is also evidenced in RAIRS after higher oxygen coverages are exposed to 0.25 L of propene at 100 K and then annealed at 200 K for 2 min (not shown).

To our knowledge, this is the first spectroscopic evidence for the formation of hydroxyl groups as propene oxidation occurs on Ag(111). This result is taken as reflecting the facile abstraction of methyl hydrogen, a process that overwhelms epoxidation and can account for the low epoxidation selectivity of propene compared to ethylene over silver catalysts.

Though the abstraction of methyl hydrogen is generally assumed to be the rate-limiting step for propene combustion on silver, the intermediate surface species are a subject of some disagreement. Carter and Goddard [4] have used generalized valence bond (GVB) theory to calculate the energetics of the elementary steps for olefin oxidation on silver and assumed allyl alkoxide ($CH_2{=}CHCH_2O_a$) as the key common surface intermediate for propene partial oxidation and combustion. In contrast, based on the experimental results from propene oxidation on Ag(110), Roberts *et al.* [7] proposed that surface allyl was the key intermediate. Recently,

Table 1
RAIRS vibrational assignments: 0.25 L $C_3H_6$ on Ag(111).

| Vibration mode[a] | Vibrational frequency (cm$^{-1}$) | | |
|---|---|---|---|
| | Clean Ag(111) | O-modified Ag(111) | Propene gas[b] |
| $\gamma_w{=}CH_2$ A″ | 908 | 913 | 912 |
| | | 924 | |
| | | 935 | |
| | | 947 | |
| $\gamma_{t,w}$ HC=CH A″ | 986 | 999 | 990 |
| $\gamma_r$ $CH_3$ A″ | 1033 | 1036 | 1045 |
| $\delta_a$ $CH_3$ A″ | 1426 | 1429 | 1442 |
| $\nu$C=C A′ | 1618 | 1610 | 1652 |
| | | 1604 | |
| $\nu_a$ $CH_3$ A″ | 2927 | 2924 | 2952 |

[a] Abbreviations: $\nu$, stretch; $\delta$, bend; $\gamma_r$, rock; $\gamma_w$, wag.
[b] Values and assignments are from ref. [22].

Hu *et al.* [5] used a dipped adcluster model (DAM) combined with *ab-initio* Hartree–Fock (HF) and second-order Møller–Plesset (MP2) calculations and drew conclusions confirming those of Roberts *et al.*

We have searched for but did not find vibrational peaks assignable to intermediate surface species. This precludes a more detailed description of the oxidation mechanism. However, our temperature-programmed reaction results tend to support surface allyl as the intermediate for propene combustion. It is known that allyl alkoxide decomposes very selectively on Ag(110) during temperature-programmed reaction to form $H_2$, acrolein ($CH_2CHCHO$), and allyl alcohol [21]. The fact that no acrolein was formed during temperature-programmed reaction of propene on O/Ag(111) for all oxygen coverages (up to saturation at 0.5 ML) argues against the existence of allyl alkoxide as an important intermediate for complete oxidation of propene (not shown). Acetone, according to theoretical calculation [5], is a product of O atom attack at the central carbon of propene accompanied by an H-atom shift. This reaction occurs in competition with further oxidation, including complete combustion, *i.e.*, to CO, $CO_2$, and $H_2O$.

## 4. Conclusions

In summary, propene oxidation on Ag(111) differs from that on Ag(110) in that partial oxidation products (acetone and CO) form in addition to the expected combustion products ($CO_2$ and $H_2O$). The first direct spectroscopic evidence (vibrational transition at $3567\,cm^{-1}$) is presented for the formation of adsorbed OH. Its formation is attributed to a reaction between methyl hydrogen of propene and oxygen adatoms, a path leading away from epoxidation. Our temperature-programmed reaction results favor the view that surface allyl is a key intermediate in propene combustion over silver catalysts.

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