Chlorine Promotion of Styrene Epoxidation on Au(111)

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In recent years, gold-based catalysts have been widely studied due to their promise as catalysts for low-temperature oxidation processes,[1,2] especially epoxidation of olefins.[3,4] Some properties of gold-based catalysts, such as low operation temperature and high efficiency, have potential for positive environmental and economic impact. Nevertheless, there are still challenges to implementing Au-based processes for epoxidation. One of these challenges is enhancement of the selectivity.

Heterogeneous epoxidation of olefins is a technologically important class of catalytic chemical reactions.[5] The current commercial catalyst used for olefin oxidation uses Ag as the active material. Selectivity for ethylene epoxidation increases from ~40 to >70% by adding chlorine.[7] Because of the many parallels between Ag and Au, we postulated that chlorine would likewise increase the selectivity for olefin epoxidation on Au.

In this communication, for the first time, we report a substantial increase in the selectivity for olefin epoxidation due to the presence of Cl on Au. By predosing chlorine, combustion of styrene and formation of organic acids are completely inhibited on O-covered Au(111). When Cl is present, there is also no residual surface carbon found after the reaction and the temperature for formation of styrene oxide is lower by ~70 K. Our model study provides strong evidence that chlorine may be an effective promoter for enhancing the selectivity of Au-based catalysts used for heterogeneous epoxidation of olefins.

As reported previously, oxidation of styrene is promoted by O-covered Au(111),[6] with styrene being selectively oxidized to styrene oxide, benzoic acid, and benzeneacetic acid during temperature-programmed reaction (Figure 1a). Styrene oxide (C_6H_5-$CHOCH_2$, $m/z = 120$, parent ion) evolved in a peak at 310 K. Benzoic acid (C_6H_5COOH, $m/z = 122$) and benzeneacetic acid ($C_6H_5CH_2COOH$, $m/z = 136$) desorbed at higher temperatures of 400 and 440 K, respectively. Combustion products, CO_2 and H_2O, formed in the range of 240−390 K. Unreacted styrene (C_8H_8, $m/z = 104$) molecularly desorbed at 230 K (multilayer) and 330 K (monolayer). Residual carbon was also detected on the surface after the reaction, indicating that there is a deficiency of oxygen and that some styrene decomposes nonselectively, further decreasing the selectivity (Figure S2). The data shown are qualitatively similar to our previous studies, although the method for oxidation of the Au is different. For experiments mentioned here, 0.3 ML of O was deposited on Au(111) using O_3 decomposition at 200 K.

To study the effect of chlorine on styrene epoxidation, the Au(111) surface was precovered with ~1.2 ML of chlorine by exposure to Cl_2 gas (Matheson Gas Inc., research grade) at 200 K. Oxygen was deposited by subsequent exposure of the surface to the same O_3 dosage that would result in a 0.3 ML oxygen coverage on clean Au(111). The presence of Cl reduces the oxygen coverage to ~0.04 ML (Figure S1), determined from the integrated area of
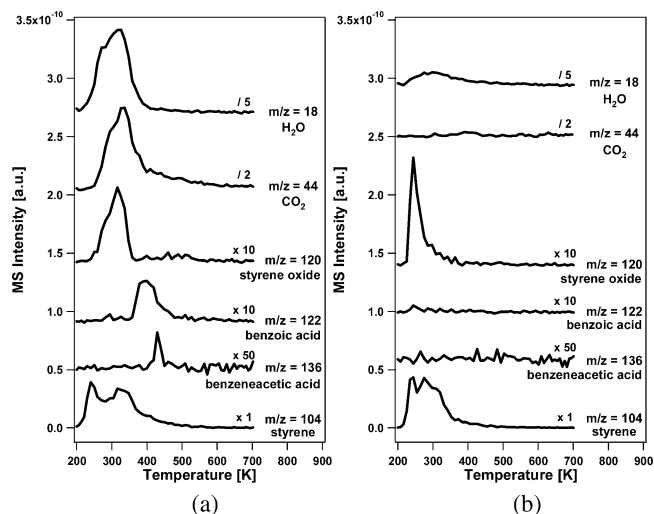
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Figure 1. Temperature-programmed reaction of styrene on (a) 0.3 ML O-covered Au(111) and (b) Au(111) with 1.2 ML predosed Cl followed by the same O_3 dosage as in (a). O_3, Cl_2, and styrene were dosed at 200 K.

the O_2 desorption trace. Styrene (Alfa Aesar, 99.5% purity) was dosed at 200 K.

When Cl and O are coadsorbed on Au(111), the selectivity for styrene epoxidation is dramatically enhanced. Nearly the same amount of styrene oxide is formed as when no chlorine is present, whereas little CO_2 is formed, and neither benzoic acid nor benzeneacetic acid is detected (Figure 1b). Styrene oxide was identified by quantitative comparison of the fragmentation pattern of the product to those measured for other geometric isomers, such as phenylacetaldehyde and acetophenone (see Supporting Information). The styrene oxide peak shifts from 310 K when Cl is absent to 240 K when it is present, indicating a ~4.8 kcal/mol decrease in the activation energy for styrene epoxidation, assuming no change in pre-exponential factors.

Production of combustion products, CO_2 and H_2O, is almost completely inhibited. The ratio of CO_2 formation in the presence and absence of Cl is 0.001:1. The small amount of H_2O detected is ascribed to background water desorption since no D_2O is formed during reaction of styrene-d_8 epoxidation when chlorine and oxygen are coadsorbed. No residual carbon was detected on the surface after reaction (Figure S2). The accumulation of residual carbon species is often considered to be the reason for deactivation of industrial catalysts.

Notably, the increase in the selectivity for epoxidation and the suppression of combustion is *not* due to the lower coverage of oxygen (Figure S1). When styrene reacts on Au(111) containing only ~0.06 ML of O_a but no Cl at 200 K, CO_2, H_2O, benzoic acid, and benzeneacetic acid are all formed, but no styrene oxide is detected (Figure S3).
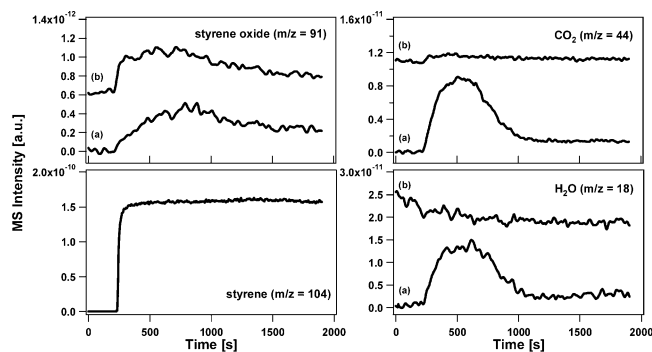
Figure 2. Reactions of styrene ($P = 1 \times 10^{-9}$ Torr) at 300 K with (a) 0.3 ML O-covered Au(111) and (b) Au(111) with 1.2 ML predosed chlorine followed by the same O_3 dosage as in (a).

Both Cl and Cl_2 evolved above 550 K with no discernible change in the Cl coverage induced by styrene oxidation (data not shown). No residual O_2 was detected, indicating that all adsorbed oxygen was consumed in the oxidation of styrene. Careful monitoring of all possible products below $m/z = 200$ confirmed that no chlorinated hydrocarbons are produced in the reaction.

Isothermal reaction of styrene at 300 K further demonstrates that the selectivity of styrene epoxidation is enhanced. In this case, O–Au(111) prepared by dosing O_3 at 300 K was exposed to styrene at a constant pressure of 1×10^{-9} Torr, which led to the immediate production of styrene oxide, CO_2, and H_2O. The production rate of CO_2 and H_2O was higher than that of styrene oxide (Figure 2a). No other products evolved at 300 K; however, benzoic and benzeneacetic acid form at 400 and 440 K, respectively, during subsequent heating to 900 K, and residual carbon was detected on the surface (Figure S4).

Chlorine substantially enhances styrene epoxidation on Au(111) under isothermal conditions at 300 K (Figure 2b). Styrene oxide, the only product detected, is produced at a higher rate when Cl is present along with O. Again, no residual carbon was detected on the surface after the reaction. There was no measurable decrease in the rate of styrene epoxidation during five consecutive reaction cycles of oxidation by O_3 and reaction of styrene on chlorine-covered Au(111) at 300 K. Clearly, on chlorine-promoted Au(111), styrene can be high selectively oxidized to styrene oxide at 300 K and the effect of Cl persists over several turnovers.

On Ag-based catalysts, the promotion of olefin epoxidation by Cl has been explained by an electronic effect, whereby Cl withdraws electron density, thus decreasing the negative charge on oxygen. As a result, electrophilic attack of the olefins by oxygen to afford the epoxide is favored, whereas the sigmatropic 1,2 H-stripping, which leads to combustion, is inhibited.[7,8]

On Au(111), we propose that a purely electronic effect does not explain the effect of chlorine on styrene oxidation reported herein. There is a shift in the peak for O_2 evolution when Cl is present— from 540 to 525 K, suggesting that there is a change in the bonding of O to Au induced by Cl. We propose that a change in the distribution and geometric arrangement of the O-covered Au surface that is induced by Cl contributes significantly to the higher selectivity for epoxidation and suppression of combustion. Recently, we reported that small Au–O clusters ($d < 5$ nm) that possibly produce mobile Au–O complexes are more active for CO and olefin oxidation than relatively ordered larger Au–O islands.[9] Both adsorbed chlorine[10,11] and oxygen[12] lift the Au(111) reconstruction

and, therefore, release Au from the surface. The presence of chlorine on the surface also reduces the oxygen sticking probability. Preliminary results of STM experiments suggest that Cl disperses Au–O complexes (Figure S5) on the surface so as to promote the addition of oxygen to styrene. Some weakening of the O–Au bond, discussed above, may also lead to the increase in epoxidation rate and corresponding decrease in the temperature for epoxide evolution. Dispersal of oxygen would also account for the suppression of multiple oxidation steps that lead to combustion, formation of organic acids, and nonselective decomposition of the styrene. Oxametallacycle species have been proposed as intermediates for styrene oxidation on Au(111)[6] and Ag(111).[13,14] On Ag, theoretical studies suggest that rearrangement of the oxymetallacycle to an aldehyde leads to combustion,[15] but there is no evidence for such a rearrangement on Au. In either case, the dispersal of oxygen on the surface induced by Cl would render secondary oxidation less likely. A second oxygen atom must be in proximity to any oxidation intermediate in order to form benzoic acid, benzeneacetic acid, CO_2 and H_2O, and residual carbon.

In conclusion, chlorine significantly enhances the selectivity of styrene epoxidation on Au(111) by inhibiting secondary oxidation, especially combustion and the deposition of residual carbon. Furthermore, the rate of styrene oxide formation is increased. Our work provides strong evidence that chlorine would be an effective promoter for enhancing the performance of Au-based selective oxidation catalysts.

Supporting Information Available: Details for the experimental section, TPD of oxygen on clean Au(111) and chlorine predosed Au-(111), post-oxidation of the surface after reaction, TPRS of styrene epoxidation on ∼0.06 ML O-covered Au(111), TPRS after isothermal reaction of styrene on O/Au(111) at 300 K, and STM images showing the dispersion of Au–O complexes by chlorine. This material is available free of charge via the Internet at http://pubs.acs.org.

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