

Insight into the liquid phase aerobic epoxidation of alkenes catalyzed by gold nanoparticles

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Introduction

Oxygenated molecules, such as epoxides, alcohols and ketones, are key-intermediates of the fine chemical industries. Activating molecular oxygen for the synthesis of these intermediates from petrochemicals is one way to making these processes cleaner [1]. Recently, we have shown that supported gold nanoparticles exhibit a unique potential for the low temperature, aerobic epoxidation of stilbene in the liquid phase [2]; this catalytic reaction is indeed 100% stereoselective towards *trans*-stilbene oxide, whether starting from *trans*- or *cis*-stilbene [3]. The activity and exceptional selectivity of the gold nanoparticles involved are however critically dependent on the use of substituted cycloalkanes as solvents and the presence of catalytic amount of *tert*-butyl hydroperoxide (TBHP) [4].

Here, we present the compared oxidation of cyclohexene and limonene under these “green” conditions. The effect of the structure of the substrate molecule on the selectivity of the gold-catalyzed reaction and product distributions obtained will be discussed.

Materials and Methods

The 1wt.%Au/C reference catalyst from the World Gold Council (Au average particle size ~ 10 nm → ~15% dispersion; activated carbon X40S from Camel; surface area ~ 1200 m²/g) is used. For catalytic evaluation, mixtures of substrate (alkene, 1 mmol) and solvent (20 mL) (or 20 mL / 123-197 mmol substrate alone for solventless reactions) are stirred (900 rpm) in air at 80°C for 24 h, in the presence or in the absence of the catalyst (40 mg / 2 μmol Au). The effect of solvent, TBHP (0.05 mmol) and flowing air (3-80 mL/min) are studied. Product identification is performed by GC-MS (Hewlett-Packard HP6890 Series); alkene conversions (C%), oxidation product yields (Y%) and selectivities (S%) are determined by GC (Shimadzu GC-2014) and HPLC (Perkin-Elmer Series 200) product analysis. Selectivity is defined as the ratio of the number of mole of product formed over the total number of mole of substrate converted. Turnover numbers (TON) are defined as the number of mole of partial oxidation product formed per mole of surface gold in 24 h.

Results and Discussion

For alkenes such as limonene, the presence of a solvent and/or TBHP in addition to the gold catalyst is detrimental to the selectivity of the reaction. In the presence of the catalyst alone, limonene oxide is formed as the major reaction product with 25% selectivity (TON ~ 12,000) at maximum conversion (12%), along with allylic oxidation products (S = 25%). Epoxidation is directed only towards the electron-rich carbon-carbon double bond. In the case of the solventless oxidation of cyclohexene, epoxide formation is minor (S < 5%); cyclohexene peroxide, cyclohexen-1-ol, cyclohexen-1-one (in a 8:4:3 molar ratio, total selectivity of 45% at

16% conversion, i.e. TON ~ 47,000) are the major products detected. Performing the reaction in an apolar solvent, such as methylcyclohexane, allows to enhance the catalytic effect and achieve selectivities up to 50%, 25 and 15%, respectively, at 27% conversion (TON ~ 800). When the incoming air flow rate is then increased from 0 to 80 mL/min, a decrease in the selectivity to partial oxidation products at iso-conversion is observed. Furthermore, at conversions >95% (achieved in 6 h at air flow rates >80 mL/min or in 24 h in polar solvents such as acetonitrile), the total selectivity to partial oxidation products falls below 5%.

While the gold-catalyzed aerobic epoxidation of stilbene requires the presence of a solvent presenting easily extractable hydrogen atoms (Figure 1),

these new results show that alkenes containing allylic hydrogen atoms, such as cyclohexene and limonene, can be selectively oxidized over supported gold nanoparticles, with high turnover numbers, *in the absence of any solvent or added peroxide*. The product distributions observed are consistent with a mechanism involving free radicals. Tuning the reaction conditions allows maximizing selective oxidation product yields whilst limiting catalyst poisoning.

Significance

This study highlights the promising potential of gold catalysts for the oxidation of alkenes with molecular oxygen. The high selectivities achieved at high conversion (as compared with those obtained with typical cobalt salts) suggest that, in addition to initiating the radical reaction, gold nanoparticles have an unexpected affinity for the radical species generated.

References

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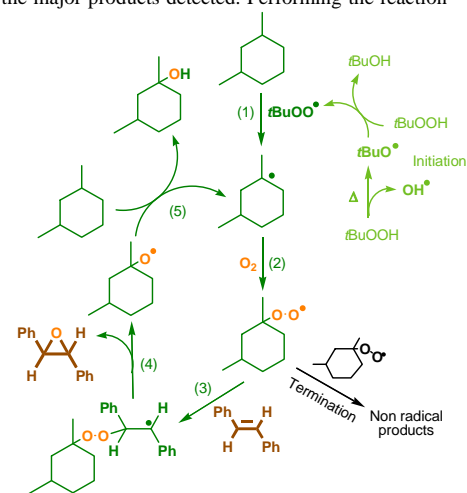


Figure 1. Proposed reaction mechanism for the gold-catalyzed epoxidation of *trans*-stilbene in dimethylcyclohexane in the presence of 0.05 mol eq. TBHP.