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Mechanistic insights into the direct propylene epoxidation using Au nanoparticles dispersed on TiO_2/SiO_2

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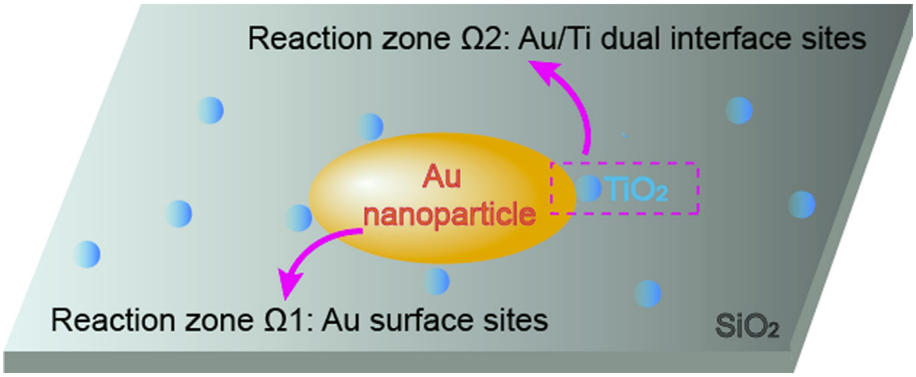
HIGHLIGHTS

- KMC simulations probe the direct propylene oxide reaction mechanism and associated byproducts.
- Propylene oxide selectivity can be enhanced by decreasing temperature and increasing H_2/C_3H_6.
- The synergistic role of Au/Ti dual interface sites is emphasized in the product formation.
- Formation of side products is correlated with the surface coverage of atomic oxygen on Au particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Direct propylene epoxidation is an important gas-phase reaction for the future industrial production of propylene oxide (PO). However, the mechanistic understanding of this reaction system is still elusive, including the role of side reactions. Herein, kinetic Monte Carlo (KMC) simulations are applied to explore the underlying mechanistic aspects of propylene epoxidation over $Au/TiO_2/SiO_2$, and consistent results are obtained with respect to experimental benchmarks. The present study systematically probes the reaction mechanism, which involves acrolein formation on Au nanoparticles as well as the formation of PO and several byproducts at the Au/Ti dual interface sites, and it highlights the synergistic effect of interface sites in heterogeneous catalysis. The origin of the negative effect of rising reaction temperature on PO selectivity has been clarified, as it is correlated with decreasing atomic oxygen coverage on the Au surface. The varying feed concentration of $H_2/O_2/C_3H_6$ leads to different coverages on the catalyst surface, emphasizing the importance of an optimum H_2/C_3H_6 inlet concentration ratio for enhancing PO selectivity and hydrogen utilization efficiency. Based on our model results, we propose that supports with acidic groups may promote hydroperoxy species transferring to the adjacent Ti sites, thereby decreasing its decomposition to atomic oxygen on the Au sites, which leads to byproduct formation.

1. Introduction

Coinage metal gold was previously regarded as a catalytically inert material. This common assumption was dramatically shifted by the discovery of low-temperature CO oxidation with

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metal oxide supported gold nanoparticles in 1987 (Masatake et al., 1987). Since that time, supported Au nanoparticles have attracted wide research interest in the field of heterogeneous catalysis, such as chemoselective hydrogenation (Corma and Serna, 2006), water-gas shift (Fu et al., 2003; Rodriguez et al., 2007), the selective oxidation of olefins (Hughes et al., 2005; Turner et al., 2008), etc. Herein, olefin oxidation, in particular propylene (C_3H_6) epoxidation to produce propylene oxide (PO), has attracted considerable attention since PO is a key intermediate for the industrial production of polyether polyols, propene glycols, and propene glycol ethers (Huang and Haruta, 2012), which are mainly used to manufacture commercial products such as foams, adhesives, and solvents (Nijhuis et al., 2006; Yap et al., 2004). Unfortunately, the current chlorohydrin process to produce PO suffers from environmental issues, and the hydroperoxide process is challenged by poor economics and the formation of byproducts. In contrast, the direct vapor-phase propylene epoxidation with molecular H_2 and O_2 catalyzed by nano-sized Au deposited on TiO_2 has been proved to be clean and highly selective. This route was first discovered by Haruta and co-workers in 1998 (Hayashi et al., 1998).

Over the past 20 years, a lot of experimental and theoretical efforts have been dedicated to improving Au-based catalysts and understanding the fundamental reaction features of direct propylene epoxidation (Chen et al., 2013a; Chen et al., 2013b; Joshi et al., 2006, 2007b; Lee et al., 2012; Nijhuis et al., 1999; Nijhuis et al., 2006; Pulido et al., 2012; Stangland et al., 2000; Wells et al., 2004a). In this system, the active oxygen species, hydrogen peroxide (H_2O_2), is readily synthesized on the anchored Au nanoparticles, and it subsequently migrates to the adjacent Ti sites to convert propylene into PO. The H_2O_2 formation via H_2 and O_2 has been investigated on a number of different surfaces, from Au particles (Barton and Podkolzin, 2005; Joshi et al., 2007a; Landon et al., 2002; Wells et al., 2004b) to other transition metal surfaces (Ni, Pd, Pt, Cu, Ag, and Rh) (Düzenli et al., 2015; Ford et al., 2010; Freakley et al., 2016; Landon et al., 2003). Despite a rising interest, the mechanistic comprehension of direct propylene epoxidation is still under intense debate. There are several controversial issues: (i) the main factors that affect the catalytic activity of nanoscale Au; (ii) the origin of the activated oxidant (Ti–OOH), and the sites that are responsible for the direct PO reaction; and (iii) the mechanistic aspects of side reactions, as well as their influence on PO selectivity and catalyst deactivation.

It is commonly believed that size and morphology are significant parameters for the catalytic activity of Au nanoparticles. For instance, estimates of the optimal Au nanoparticle size for propylene epoxidation, have reduced from 2 to 5 nm in the early studies of Haruta and Daté (2001) and Hayashi et al. (1998) to sizes smaller than 2 nm in diameter (Huang and Haruta, 2012; Huang et al., 2010; Okumura et al., 2015). In contrast, both density functional theory (DFT) calculations and indirect experimental evidence have suggested that tiny Au clusters (composed of a few atoms) incorporated in microporous channels (~0.55 nm) of TS-1 could be responsible for the high activity (Huang and Haruta, 2012; Joshi et al., 2006, 2007b; Lee et al., 2012; Yap et al., 2004). The activity of Au nanoparticles has been ascribed to quantum size effects (Valden et al., 1998), high step-density and strain on Au nanoparticles (Mavrikakis et al., 2000), and charge-transfer due to electronic interactions between particles and oxide supports (Yoon et al., 2005). However, H_2 dissociation experiments have revealed that the most active sites are gold atoms in contact with the TiO_2 support, which further support the hypothesis that the Au/support interface is crucial for the formation of active sites (Fujitani et al., 2009). In short, the unusual activity of nanometer-sized Au particles is still an open question, and no consensus has been reached to date.

Hydrogen peroxide formation on Au nanoparticles is viewed as a key reaction step prior to its spillover onto a TiO_2 support, leading to the formation of metal peroxo compounds (Ti–OOH species) (Bravo-Suárez et al., 2008; Hayashi et al., 1998; Uphade et al., 2002; Wells et al., 2004a). Theoretical calculations have predicted the existence of H_2O_2 on Au particles (Olivera et al., 1994; Wells et al., 2004a,b), whereas experimental verification has been challenging, since H_2O_2 is unstable and easily decomposes into water at high temperature (Lee et al., 2012). Thus, whether H_2O_2 is just a spectator or a reactive species is obscured. Even though the H_2O_2 intermediate is known to be an active species, its lifetime on an Au/TiO_2 surface is unknown, and it may degrade before reaching the Ti sites. Recently, an inelastic neutron scattering (INS) study (Sivadinarayana et al., 2004) and an in situ UV spectroscopy study (Chowdhury et al., 2006) offered direct spectroscopic evidence for the formation of H_2O_2 and the hydroperoxy radical (OOH) species, originating from H_2-O_2 related reactions over Au/TiO_2. Furthermore, both experimental and theoretical studies regarding the propylene epoxidation with a mixture of O_2/H_2O indicated that, instead of H_2O_2, it is the OOH radical ($O_2^* + H_2O^* \leftrightharpoons OOH^* + OH^*$, where $*$ stands for the adsorbed species) that directly migrates to the neighboring Ti site to form Ti–OOH species, resulting in PO production (Chang et al., 2015; Chang et al., 2011; Liu et al., 2016; Ojeda and Iglesia, 2009). Nonetheless, the active oxidizing species is still unverified (OOH^* or $H_2O_2^*$) due to the absence of transient kinetic data. In addition, there are different opinions about the active sites for the epoxidation reaction. A reasonable proximity between Au and Ti sites is generally considered to be indispensable for the PO reaction, suggesting the existence of a well-defined reaction zone (Driscoll et al., 2017; Fujitani et al., 2009; Joshi et al., 2007b; Lee et al., 2012; Panayotov et al., 2016; Taylor et al., 2006; Yap et al., 2004). However, several DFT studies have suggested that single gold particles can catalyze propylene epoxidation without the participation of Ti sites (Joshi et al., 2006; Moskaleva, 2016).

Gold-titania systems are able to catalyze propylene epoxidation with a mixture of H_2/O_2 under very mild conditions (atmospheric pressure and 323–393 K) and exhibit high PO selectivity (>99%) (Nijhuis et al., 2005b; Stangland et al., 2000). Despite the high selectivity of the gold-titania catalysts, the propylene conversion is typically low (<2%) and the hydrogen efficiency (<30%) is insufficient (Nijhuis et al., 2005b; Zwijnenburg et al., 2004). Attempts to improve propylene conversion by raising the reaction temperature, inevitably lead to decreasing PO selectivity due to consecutive PO reactions (isomerization, oligomerization, and oxidative cracking) (McEntee et al., 2015; Moskaleva, 2016; Okumura et al., 2015; Stangland et al., 2000; Uphade et al., 2002). These secondary reactions generate byproducts such as propanal, acetone, ethanal, CO_2, dioxane, and acids. It is worth noting that acrolein is another significant byproduct (Stangland et al., 2000). The allylic hydrogen of propylene is acidic and labile, and easily suffers from the nucleophilic attack of the oxygen radicals bound to Au nanoparticles, since the oxygen species behave as a Brønsted base (Baker et al., 2011; Dai et al., 2017; Wells et al., 2004a; Yap et al., 2004). Friend and Moskaleva have identified acrolein formation on the Au surface, but with different intermediates (Deng et al., 2006; Liu and Friend, 2010; Moskaleva, 2016). Additionally, in situ fourier transform transmission infrared spectroscopy (FTIR) combined with DFT calculations highlighted the ketenylidene ($Au_2C{=}C{=}O$) formation from propionic and acetic acids at the Au/TiO_2 perimeter sites (Green et al., 2012; McEntee et al., 2015). Nevertheless, detailed information with respect to side reaction pathways is limited, which limits our ability to suppress undesired byproduct formation.

In this work, kinetic Monte Carlo (KMC) simulations are performed to simulate the chemical kinetics of direct propylene