

Drifts study of the gas-phase epoxidation of propene over Au/TiO₂ catalysts

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Introduction

The gas phase epoxidation of propene is a promising process to replace the conventional propylene oxide manufacturing methods that have economical and ecological disadvantages. In 1998, Haruta et al. found that highly dispersed Au/TiO₂ catalysts were selective for the epoxidation of propene in the presence of oxygen and hydrogen, obtaining propylene oxide with selectivities higher than 90 % and conversions of 1-2 % [1]. Although Au/TiO₂ catalysts are very selective for the direct propene epoxidation reaction, their activity and stability are usually low. The mechanistic pathway and route to deactivation of the epoxidation reaction over gold-titania catalysts are still under discussion. It has been reported that hydrogen and oxygen can react on small gold particles to form hydroperoxide-like species, which then further react with propene to produce propene oxide [2,3]. The presence of peroxide species on Au/TiO₂ catalysts has recently been demonstrated by Oyama et al., providing evidence that Ti-hydroperoxo species are true intermediates in the direct epoxidation of propene [4]. On the contrary, Nijhuis et al. observed that propene was adsorbed on Au/TiO₂ to produce bidentate propoxy species and these authors considered this species to be a reaction intermediate in propylene oxide formation [5]. Elucidation of reaction pathways will be key to improve the catalytic performance of gold-titania catalysts and to make them attractive for application in a large-scale process. Therefore, Diffuse-reflectance infrared fourier transformation spectroscopy (DRIFTS) has been used to investigate the interaction of reactants (propene, hydrogen and oxygen) and products (propylene oxide) with Au/TiO₂ catalyst, to reveal the mechanism of the direct propene epoxidation over Au/TiO₂ catalysts.

Experimental

Degussa P-25 titania was the standard support material used to prepare Au/TiO₂ material. Catalysts containing 1 % wt. Au were prepared by deposition-precipitation of Au(OH)₃ at pH 9.5 and ambient temperature. The catalyst was calcined at 400 °C for 4 h.

DRIFTS experiments were performed on a Thermo Nicolet Nexus IR with OMNIC software, connected to a Pfeiffer Vacuum TermoStar mass spectrometer. For reaction experiments a mixture of 10 % propene, 10 % H₂, 10 % O₂ and 70 % He was used at 50 °C.

Results and discussion

The spectra obtained upon propene adsorption on, and subsequent desorption from the Au/TiO₂ catalyst are shown in Figure 1. The interaction of propene with the catalyst is not completely reversible. Absorptions in the 1700 to 1300 cm⁻¹ region are attributed to acrylate ions [7]. The signals at 1550 and 1437 cm⁻¹ can be assigned to asymmetric and symmetric O-C-O stretching vibrations of acrylate, respectively. Over time, the intensity of the characteristic

absorptions of acrylate decreased, with remaining bands at 2930, 2866, 1576, 1471, 1438 and 1371 cm⁻¹ that can be attributed to a mixture of formate and carbonate species. It should be noted that the interaction of propene with the titania P25 support in the absence of gold was reversible, suggesting that gold promotes partial oxidation of propene in small quantities.

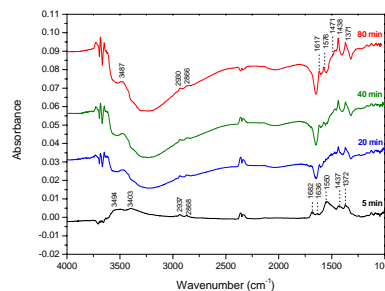


Figure 1. DRIFTS spectrum of Au/TiO₂ catalyst recorded in He at 323 K (5-80 min) after 20 min of propene adsorption.

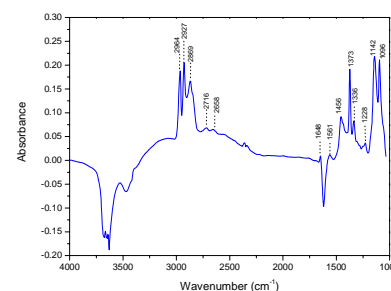


Figure 2. DRIFTS spectrum of Au/TiO₂ catalyst recorded in He at 323 K (60 min) after 45 min of 1,2-propanediol adsorption

The adsorption of 1,2-propanediol and PO over Au/TiO₂ catalyst was performed, obtaining the spectra that are shown in Figure 2. Species formed in the 1,2-propanediol (and PO, not shown) experiment are quite different from those obtained for propene adsorption/desorption and are assigned to bidentate propoxy species. After adsorption and subsequent desorption of 1,2-propanediol, a mixture of H₂ and O₂ was added to the catalyst to elucidate the role of bidentate propoxy species in the gas-phase epoxidation reaction. The presence of H₂ and O₂ did not induce changes in the spectra of the surface bidentate propoxy compound, and characteristic absorptions of propylene oxide were not observed. The implications of these observations for the mechanism proposed by Nijhuis et al., as well as our earlier studies [7], will be discussed.

Conclusions

Propene adsorbed on Au/TiO₂ can be transformed to minor quantities of an acrylic intermediate, a precursor of formate and carbonate species. This last step should be considered as the reaction step towards catalyst deactivation and not to an intermediate for production of PO.

References

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