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Gold Catalyzed Propene Epoxidation – A study in Catalytic Activity and Reaction Mechanism

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Introduction
Gold–titania catalysts form a very attractive alternative for the direct epoxidation of propene compared to the traditional process as it is a one step- environmentally benign process. In the presence of hydrogen and oxygen, propene can be directly epoxidized to propene oxide (PO) over a gold–titania catalyst with very high selectivity (close to 100 %) with only water as the major side product [1]. Some of the factors that have kept this process from replacing the conventional one are its low conversion and H₂ efficiency. The exact reaction mechanism is also still a matter of debate [2]. Studies by our group have proved the importance of the synergy between Au and Ti in catalytic activity and also found an interesting feature that low gold loaded catalysts seem to have a unique high activity [3].

In this work, the influence of low gold loading has been studied on two different titano-silicate supports: Ti grafted on an amorphous silica (denoted as TiSiO₂) and the zeolite, TS-1. The effect of gold loading on catalytic activity, H₂ efficiency and stability has been studied at different temperatures. Thereafter, a thorough kinetic study was performed which included the influence of the concentration of reactants, reaction temperature and residence time. A reaction mechanism based on fundamental reaction steps at the catalyst surface was proposed to explain this experimental data. The rate expressions for PO and water formation were developed based on this mechanism. Finally the model was fitted to the extensive kinetic data generated.

Materials and Methods
Two titano-silicate supports were synthesized as outlined in [3]. The gold deposition was carried out using deposition-precipitation method with gold precursor, H₂AuCl₄, at pH 9.5 in case of TiSiO₂ and 7.3 for TS-1. All gold loadings were kept <0.2wt%. The catalysts were characterized using UV-Vis, TEM, SEM, ICP-OES and XRD.

The catalytic activity testing was carried out in a flow setup equipped with online GC at GHSV of 10000-14000 mL/gcat/h, over temperature range 423-500K with H₂/O₂/C₃H₆/He=1:1:1:7. Each catalytic cycle was 5 hours in duration interspersed with a re-calcination step at 573K in O₂/He. The kinetic tests were performed at 473K with 5 hour reaction cycle followed by re-activation, on the most active catalysts with the variation of the concentration of each reactant such that the mixture is always in the non-explosive regime. The data fitting on the kinetic model was done with the aid of the software Athena Visual Studio.

Results and Discussion
A series of Au/TiSiO₂ and Au/TS-1 were synthesized and their catalytic activity was studied. It was found that not only does the low gold loading ~0.1wt%Au show exceptionally high activity (125-150 gPO/gcat·h⁻¹, at 220C), but also increases the H₂ efficiency significantly. Figure 1 shows the influence of Au loading on these two parameters for Au/TS-1. Similar trends were observed for Au/TiSiO₂ as well. The gold nanoparticles were invisible to conventional TEM leading us to believe that their size is <1nm [4].

A reaction mechanism was proposed which assumes that there are two types of Au sites: isolated, which form only water and the ones in the vicinity of Ti which form PO as well as water. The active species on both is OOH*, the decomposition of which leads to water formation and when it spills over to Ti sites and combines with propene it results in PO formation. This scheme is shown in Figure 2. An extensive kinetic data set was generated (by varying the concentration of each reactant) which was found to fit well with the rate equations derived from this mechanism.

Significance
Highly active catalysts with improved H₂ efficiency were prepared on two different supports for the direct epoxidation of propene. This brings us one step closer to making this process economically viable. The proposed mechanism successfully quantifies the formation of both PO and water on these catalysts.

References

Figure 1. Influence of gold loading on rate of PO formation and H₂ efficiency (%) for Au/TS-1(100) catalysts at 473K, (H₂/O₂/C₃H₆/He=1:1:1:7; GHSV 14 000 mL/gcat/h) *Loading in solution

Figure 2. Schematic representation of model for PO and water formation in propene epoxidation over gold titania catalyst