

Towards highly stable and active Au/uncalcined TS-1 catalysts for direct propylene epoxidation with molecular H₂ and O₂: Effect of Si/Ti molar ratio

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Introduction

Propylene oxide (PO) is recognized as a high value-added chemical intermediate for manufacturing of polyurethane and polyether resins. In contrast to the traditional chlorohydrin process and several organic hydroperoxide processes, direct propylene epoxidation with H₂/O₂ for PO synthesis is more attractive because it is environmental friendly and simple. For this reaction, Ti-containing material (e.g., TS-1 and Ti-SiO₂) supported Au catalysts are indispensable for PO synthesis, and Si/Ti molar ratio of the Ti-containing support is critical for the catalytic performance. However, there is still debate on the optimum Si/Ti ratio (e.g., 100 and 35), which is highly desired for the rational design of efficient Au/Ti-containing catalysts [1]. Herein, reduced Au/TS-1 catalysts with different Si/Ti ratio are studied by HRTEM/BET. The results show that the difference in the activities of the Au/TS-1 catalysts with different Si/Ti ratios is mainly due to the different amounts of highly active tiny Au clusters inside the microporous channels, which is confirmed by the In-situ UV-vis experiment of the hydrolysis process of Au precursors. We then use nonporous uncalcined TS-1 support (TS-1-B) [2] to unravel the entangled effect of Si/Ti ratio. Subsequently, the Au/TS-1-B catalysts are further optimized, and show remarkably improved activity and stability compared with traditional Au/Ti-containing catalysts that usually suffer from severe catalyst deactivation.

Materials and Methods

Au nanoparticles were deposited on traditional TS-1 with open micropores (TS-1-O) and uncalcined TS-1 with blocked micropores (TS-1-B) by deposition-precipitation method [1]. The catalytic testing for the gas-phase propylene epoxidation was carried out in a quartz tubular reactor using a feed concentration of 10/10/10/70 vol.% of C₃H₆, H₂, O₂ and N₂ (at a space velocity of 14,000 mLh⁻¹g_{cat}⁻¹) at 1 atm with 0.15 g catalysts.

Results and Discussion

Au/TS-1-O(100) and Au/TS-1-O(35) catalysts with the same loading of 0.10 wt% are tested for direct propylene epoxidation and characterized by HRTEM and BET techniques. The Au/TS-1-O(100) catalyst exhibits higher activity owing to more tiny and active Au clusters residing in the microporous channels (ca. 0.55 nm). This is confirmed by the In-situ UV-vis measurement of the hydrolysis process of Au precursors. With longer Au slurry aging time, more Au precursors with smaller steric hindrance (e.g., [AuCl(OH)₃]⁻) are allowed to enter into the microporous channels of TS-1(100). The scheme is shown in **Figure 1**. Therefore, the nonporous TS-1-B support are used to deposit Au nanoparticles to exclude the effect of tiny Au clusters inside the channels, and Si/Ti ratio of 35 is demonstrated to be

superior towards PO synthesis, a possible reason for this is that more Ti-OOH reaction intermediates facilitate the epoxidation of propylene. Moreover, optimization of the catalytic performance of Au/TS-1-B catalyst based on above results is also performed. The 0.13 wt% Au/TS-1-B(35) catalyst shows significantly enhanced catalytic activity of 160 g_{PO}h⁻¹kg_{Cat}⁻¹ and stability over 30h compared with traditional Au/TS-1-O catalysts without adding promoters (**Figure 2a**). The Au/TS-1(35) catalyst could also be regenerated for several times and used for 1000 h (**Figure 2b**).

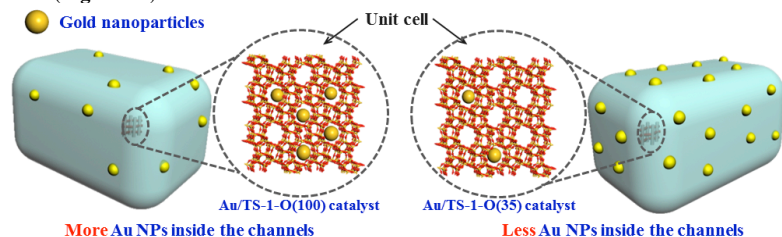


Figure 1. Schematics of Au locations of the reduced Au/TS-1-O catalysts.

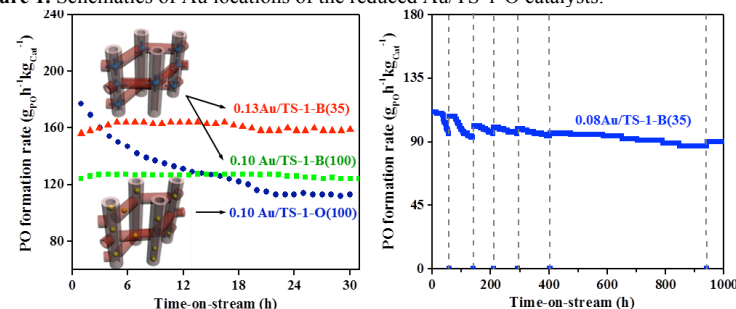


Figure 2. The activity of Au/TS-1-O and Au/TS-1-B catalysts (a), and regeneration test of 0.08 wt% Au/TS-1-B (b). The insets in Figure 2a are framework structures of TS-1-O and TS-1-B, and the dashed line in Figure 2b represents the regeneration process.

Significance

It is demonstrated in this work that the debatable effect of Si/Ti ratio on the catalytic activity results from the different amount of highly active tiny Au clusters inside the microporous channels. By employing the nonporous uncalcined TS-1(TS-1-B) as support, we exclude the influence of tiny Au clusters inside the channels and confirm that the optimal Si/Ti ratio is 35. The optimized Au/TS-1-B catalyst shows significantly enhanced activity and stability than traditional Au/Ti-containing catalysts. It can be easily regenerated and used for over unprecedented 1000 h.

References

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