

## Manipulating the architecture of titanium silicalite-1 supported Au catalysts for direct propene epoxidation with H<sub>2</sub> and O<sub>2</sub>

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### Highlights

- Micropore blocking is the main deactivation mechanism for propene epoxidation.
- Precise manipulation of Au spatial location on support can effectively enhance stability.
- Size-dependent activity and active sites are identified using unique Au/uncalcined TS-1.
- The Au/TS-1 has been tested for 1000 h, which is promising for industrial application.

### 1. Introduction

Propylene oxide (PO) as the third largest propylene derivative, is recognized as a high value-added chemical intermediate for manufacturing of polyurethane and polyether resins [1]. The green and simple production of PO by direct propylene epoxidation with H<sub>2</sub> and O<sub>2</sub> has attracted worldwide attention. Among the commonly used bi-functional Au/Ti-containing catalysts, Au/TS-1 catalyst exhibits superior catalytic performance. However, it always suffers from severe deactivation and poor conversion (i.e., lower than 5%)[2]. Therefore, it is of prime scientific and industrial importance to elucidate the structure-performance relationship in order to design a highly efficient catalyst for propene epoxidation with H<sub>2</sub> and O<sub>2</sub>.

In this work, the deactivation mechanism (e.g., pore blocking, site coverage or Au aggregation) was first discriminated. Based on the deactivation mechanism (micropore blocking), novel strategies to manipulate the spatial distribution of Au on TS-1 support and to improve the mass transfer ability were further developed, which are both effective in enhancing stability of Au/TS-1 catalysts. Moreover, accurate size-dependent activity and active sites of Au/TS-1 catalyst were studied by model calculation. The designed Au/TS-1 catalyst can be used and regenerated over 1000 h, which is promising for industrial application.

### 2. Methods

The TS-1 support was synthesized by hydrothermal method[3]. In a typical process, titanium (IV) tetrabutoxide (TBOT) dissolved in isopropanol was added drop-wise to the mixture of tetraethylorthosilicate and tetrapropylammonium hydroxide (TPAOH). The gel was crystallized at 443 K for at least 18 h. The products with and without further calcination were named as TS-1 and Un-TS-1, respectively. Novel nanosized mesoporous TS-1 is prepared by the dry-gel conversion method[1].

### 3. Results and discussion

#### 3.1 Elucidation of deactivation mechanism.

Aggregation of Au is normally regarded as the deactivation mechanism for Au catalysts. However, average sizes of Au NPs on Au/TS-1 catalysts at 4 and 30 h are almost the same. Therefore, carbonaceous deposits formation on different catalysts sites may be deactivation mechanisms (e.g., active site coverage and/or the pore blocking), which can be discriminated by an analysis of relative changes in the pore volumes and volumes of carbonaceous deposits (Figure 1). The

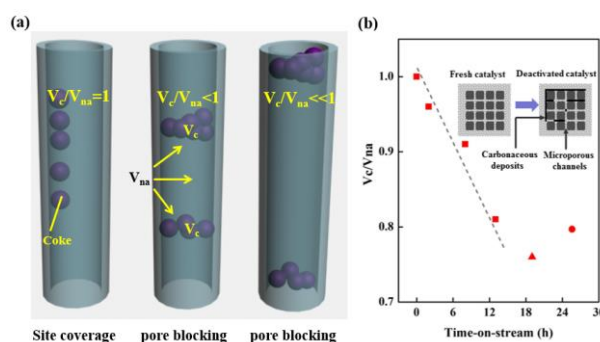


Figure 1. The method to discriminate deactivation mechanism.

decrease of  $V_c/V_{na}$  from 1.0 to 0.75 demonstrates that micropore blocking is the deactivation mechanism.

### 3.2 Strategies to enhance stability by precise Au spatial control and increased mass-transfer ability.

Based on the micropore blocking deactivation, two strategies were developed. 1) Depositing Au nanoparticles on the external surfaces of TS-1 support. This can be achieved using Un-TS-1 support whose microporous channels are occupied by TPA template (Figure 2a). As expected, the Au nanoparticles on the external surfaces of TS-1 cannot be blocked by the carbonaceous deposits inside micropores, and the catalyst exhibits good stability and higher stable activity than reported catalysts. 2) Enhancing mass-transfer ability of TS-1 support by synthesizing nano-sized TS-1 (MTS-1, <100 nm) with mesopores (ca. 3 nm) (Figure 2b). This Au/MTS-1 catalyst shows simultaneously enhanced PO selectivity (>95%) and high stability over 48 h, which are much better than traditional Au/TS-1 catalysts. The reason for the better performance is mainly attributed to enhanced mass transfer ability by shortened reactant/product diffusion length and also better hydrophobicity, which result in reduced coke weight and absence of aromatic coke[3-4].

### 3.3 Identification of size-dependent activity and active sites.

Propene epoxidation with  $H_2$  and  $O_2$  is a typical structure-sensitive reaction. The identification of intrinsic size-dependent activity of Au catalyst was achieved over stable Au catalysts with distinguishable and uniform-sized Au particles, which are critical for structure-sensitivity analysis. The PO formation rate over these catalysts was found to vary with average Au diameter ( $d$ ) as  $d^{-2.7 \pm 0.3}$ . Moreover, typical Au nanoparticles appear as truncated cuboctahedron with top facet of (111). Model calculations derived from the representative Au particle shape and the above size-dependent activity were then performed to show that corner sites of Au nanoparticles are dominant Au active sites[5-6]. Moreover, the designed Au/TS-1 catalysts can even be used and regenerated over 1000h.

## 4. Conclusions

To sum up, this paper not only elucidates the deactivation mechanism, but also proposes two strategies to enhance catalytic stability. Moreover, it identifies the intrinsic size-dependent activity and active sites of catalysts. The designed catalyst can even be used and regenerated over 1000h, which is promising for industrial application. This work bridges science and technology, and is of referential importance to the design of highly stable metal/zeolite catalysts.

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## Keywords

Structure-performance relationship; Propene epoxidation; Deactivation; Mass transfer

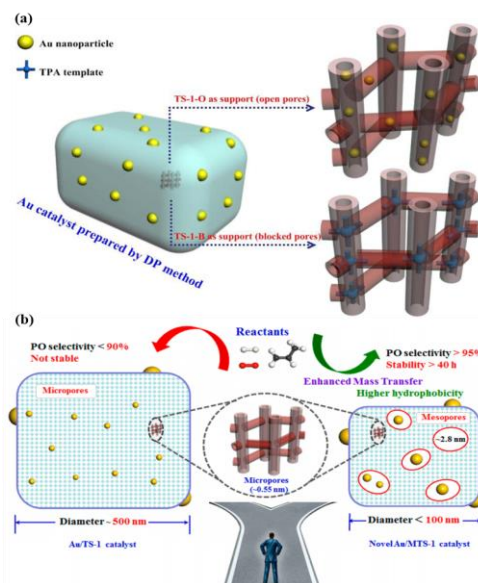


Figure 2. Strategies to enhance the catalytic stability.

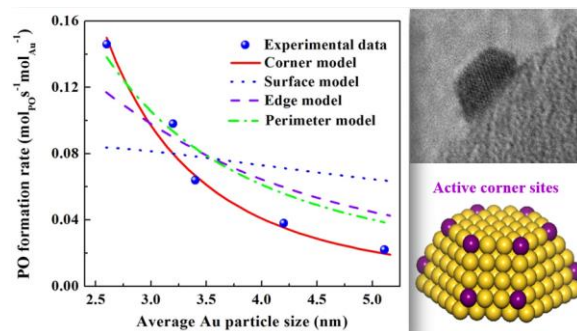


Figure 3. Identification of size dependence and active sites.

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## Education and Professional Experience

|                     |                            |                      |                     |
|---------------------|----------------------------|----------------------|---------------------|
| Sept.2017-present   | Norwegian U of Sci & Tech  | Chemical Engineering | Post-doc            |
| Mar.2017-present    | China U of Petroleum       | Chemical Engineering | Associate Professor |
| Mar.2015-Mar.2017   | China U of Petroleum       | Chemical Engineering | Post-doc            |
| Sept.2010-Mar.2015  | East China U of Sci & Tech | Chemical Engineering | PhD                 |
| Sept.2006-June.2010 | East China U of Sci & Tech | Chemical Engineering | Bachelor            |

**Dissertation:** *Design and optimization of highly stable and active Au/titanium silicalite-1 (Au/TS-1) nanocatalysts for propene epoxidation with H<sub>2</sub> and O<sub>2</sub> and the structure-performance relationship* (Supervisor: Prof. **Xinggui Zhou**, **Weikang Yuan**; Co-supervisor: Prof. **De Chen**, Norwegian U of Sci & Tech)

- ✓ Proposing the deactivation mechanism of Au/TS-1 catalyst (i.e., micropore blocking by coke).
- ✓ Selectively depositing Au nanoparticles on the external surfaces of support to enhance the stability.
- ✓ Synthesizing nano-sized hierarchical TS-1 with increased mass transfer by dry-gel conversion method.
- ✓ Identifying the size-dependent activity and predicting the active sites on gold using model calculations, characterizations and experiments.
- ✓ The designed Au/TS-1 catalyst can be used over 1000 h. (Pilot plant trial).
- ✓ Scaling up the cost-efficient synthesis of titanium silicalite-1 for industrial application.

### Research topic:

- ✓ Catalytic cracking of heavy oil to light olefin (by experiments and DFT calculation).
- ✓ Selective oxidation of light olefin (e.g., propene) to epoxide on TS-1 catalyst.
- ✓ Synthesis and scale-up of new zeolite materials (e.g., TS-1, ZSM-5 and beta).

Currently running 10 projects from NSFC and the government with a funding of ca. 2 Million RMB.

## Represented Publications

- [1] **X. Feng**, N. Sheng, Y.N. Liu, X.B. Chen, D. Chen, C.H. Yang\* and X.G. Zhou\*, Simultaneously Enhanced Stability and Selectivity for Propene Epoxidation with H<sub>2</sub> and O<sub>2</sub> on Au Catalysts Supported on Nano-crystalline Mesoporous TS-1, *ACS Catalysis*, 2017, 7(4), 2668-2675.
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## Patents

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## Honors

- ✓ **Oral presentation award** of 23rd international symposium on chemical engineering (**ISCRE 23**);
- ✓ **First prize in adolescents science & technology innovation contest** (Top 2%) of Shanghai;
- ✓ **Second prize in technology invention prize** of universities in Shanghai;
- ✓ **Tomorrow's tech star nomination award** of Shanghai;
- ✓ **High-level personnel** of Qingdao, 2017;
- ✓ Second prize in **East China mitsui chemicals cup chemical designing contest**; **National scholarship** for twice; Shanghai chemical industry park innovation and technology scholarship.