Supporting information for

Highly stable TS-1 extrudates for 1-butene epoxidation through improving the heat conductivity

Tonghui Li¹, Yi Zuo¹,*, Yuzhou Guo¹, Hong Yang², Min Liu¹, Xinwen Guo¹,*

¹ State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China.

² Laboratory for Functional Materials, Department of Mechanical Engineering, The University of Western Australia, Perth, WA 6009, Australia.

*Corresponding Authors:

Y. Zuo. Tel.: +86 411 84986486. Fax: +86 411 84986134. E-mail: zuoy@dlut.edu.cn.

X. Guo. Tel.: +86 411 84986133. Fax: +86 411 84986134. E-mail: guoxw@dlut.edu.cn.
Chart S1. The flow chart of the fixed-bed reactor.

Table S1. The highest temperature in different catalyst bed.

<table>
<thead>
<tr>
<th>Cat.</th>
<th>Temp. / K</th>
<th>Cat.</th>
<th>Temp. / K</th>
<th>Cat.</th>
<th>Temp. / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1/SiO₂</td>
<td>318.2</td>
<td>TS-1/0.1Fe</td>
<td>319.0</td>
<td>TS-1/0.1Cu</td>
<td>317.5</td>
</tr>
<tr>
<td>TS-1/0.1SiC</td>
<td>318.8</td>
<td>TS-1/0.2Fe</td>
<td>319.2</td>
<td>TS-1/0.2Cu</td>
<td>317.2</td>
</tr>
<tr>
<td>TS-1/0.2SiC</td>
<td>319.5</td>
<td>TS-1/0.3Fe</td>
<td>318.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS-1/0.3SiC</td>
<td>318.9</td>
<td>TS-1/0.4Fe</td>
<td>318.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS-1/0.4SiC</td>
<td>318.3</td>
<td>TS-1/1.0Fe</td>
<td>318.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS-1/0.5SiC</td>
<td>317.9</td>
<td>TS-1/1.5Fe</td>
<td>317.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
*The temperature was obtained at the initial stage after the adsorption heat was released.

It is usually considered that the internal diffusion limitation is eliminated when the reactant conversion is not influenced by the particle size. It can be seen from the table below that the H$_2$O$_2$ conversion ($\chi$(H$_2$O$_2$)) over the catalyst with a size of 20-40 mesh is similar to that of 40-60 mesh, but higher than that of 10-20 mesh. Therefore, the internal diffusion limitation was considered to be eliminated when the particle size was smaller than 20-40 mesh.

**Table S2. Experiments of eliminating the external and internal diffusion limitation.**

<table>
<thead>
<tr>
<th>Particle size / mesh</th>
<th>$\chi$(H$_2$O$_2$) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40-60</td>
<td>74.8</td>
</tr>
<tr>
<td>20-40</td>
<td>74.9</td>
</tr>
<tr>
<td>10-20</td>
<td><strong>70.1</strong></td>
</tr>
</tbody>
</table>

Reaction conditions: 313 K, 3.2 MPa, molar ratio of 1-butene to H$_2$O$_2$ is 3/1 and the WHSV of 1-butene is 0.87 h$^{-1}$. The data were the average values of the first 24 h.
A nanosized TS-1 synthesized according to the improved conventional method was introduced as a reference.\textsuperscript{S1} The typical synthesis process was adding tetraethyl orthosilicate (15.0 g), tetratripropylammonium hydroxide solution (25 wt\%, 16.8 g) and water (4.2 g) to a 100 mL flask and hydrolyzing the mixture at 313 K for 5 h. The solution of tetrabutyl titanate (0.7 mL) in isopropyl alcohol (5.8 mL) was then added to the resultant clear solution. Finally, water (18.0 g) was added to the above clear solution. The mixture was then crystallized at 433 K for 12 h under autogenous pressure. The solid was separated by centrifugation, washed with distilled water, dried at 373 K overnight and calcined at 813 K for 6 h. The obtained TS-1 powder was denoted as CTS-1. It can be seen that the intensities of the five characteristic peaks of CTS-1 are much stronger than those of the extruded samples, which is due to the introducing of amorphous silica by extrusion reducing the content of TS-1 relatively.

Figure S1. TG curves of the spent SiC-added TS-1 catalysts.

Figure S2. XRD patterns of the SiC-added TS-1 catalysts (a) and SiC (b).
Figure S3. FTIR (a) and UV/vis (b) spectra of SiC and the SiC-added TS-1 catalysts.

Figure S4. Nitrogen physisorption isotherms of the SiC-added TS-1 catalysts.

The SEM images of TS-1/0.4SiC at different resolutions (Figs. S5e, S5h and S5i) show that the TS-1 particles (yellow), which are adhered by amorphous silica (blue), cover on the big SiC particles (red).
The XRD patterns of Fe-added TS-1 extrudates are shown in Fig. S6a. The intensities of the XRD peaks decrease with the increased Fe content in the samples. Fig. S6b shows the XRD patterns of the Fe powder before and after calcined at 813 K for 6 h. The Fe converts to FeO$_x$ during the calcination. However, the peaks of FeO$_x$ are absent in all the iron doped samples, indicating that the FeO$_x$ species are well dispersed in the extrudates.
The FTIR and UV/vis spectra of the Fe-added samples are shown in Fig. S7. The content of framework Ti seems not affected by the addition of Fe, since the relative intensities of the bands at 960 cm\(^{-1}\)/800 cm\(^{-1}\) in FTIR spectra of all the samples are nearly the same. The introducing of Fe leads to a wide absorption at near UV and visible light region. The intensity of the band between 300 and 800 nm increases with the Fe content obviously.

The nitrogen physisorption isotherms of Fe-added samples also maintain the type I curves,
indicating that micropores are dominated in them (Fig. S8). Furthermore, the addition of Fe leads to the decrease of the uptake at the $p/p_0$ of 0.6-1.0, which is assigned to the macropores generated from the removal of Sesbania powder during the extrusion.

Figure S8. Nitrogen physisorption isotherms of the Fe-added TS-1 catalysts.

Figure S9. SEM images of the Fe-added TS-1 catalysts.
The XRD patterns of the Cu-added samples (see Fig. S11) illustrate that the diffraction peak of elementary Cu ($2\theta = 43.4^\circ$) appears in both samples, and the intensity of the peak positively relates to the content of Cu. Thus, we inferred that the structure of Cu was not destroyed during the extrusion.

The FTIR and UV/vis spectra of the Cu-added samples are shown in Fig. S12. The framework
Ti content is still not affected by the addition of Cu, according to the relative intensity of 960 cm$^{-1}$/800 cm$^{-1}$ in FTIR spectra and the band at 210 nm in UV/vis spectra. It is also clear that the absorbance for visible light increase significantly, due to the addition of Cu.

![FTIR spectra of Cu-added TS-1 catalysts](image1)

Figure S12. FTIR (a) and UV/vis (b) spectra of the Cu-added TS-1 catalysts.

The nitrogen physisorption isotherms of the Cu-added catalysts (Fig. S13) are nearly the same, since the addition of such a small amount of Cu does not destroy the structure of TS-1.

![Nitrogen physisorption isotherms](image2)

Figure S13. Nitrogen physisorption isotherms of the Cu-added TS-1 catalysts.
Figure S14. SEM images of the Cu powder and Cu-added TS-1 catalysts.

Figure S15. EDS analysis of TS-1/0.2Cu.
With the increase of additive amount, the relative content of TS-1 in the catalyst decreases gradually. The WHSV of 1-butene was calculated based on the weight of catalyst, but not TS-1, so the content of TS-1 may affect the catalytic performance. Therefore, the WHSV of 1-butene was changed to study the effect of TS-1 content on the catalytic performance. The TS-1/0.1SiC was used for the comparative experiment. The WHSV of 1-butene used for TS-1/0.1SiC and TS-1/0.5SiC was 1.16 and 1.26 g/(g_{TS-1}·h), respectively, based on the weight of TS-1. Thus, the catalytic performance over TS-1/0.1SiC was evaluated at the 1-butene WHSV of 1.26 g/(g_{TS-1}·h). The other conditions were not changed.

The results in Fig. S17 shows that the H_{2}O_2 conversion and BO selectivity are quite similar under the two conditions, indicating that the increase of WHSV has little effect on the catalytic performance.
Figure S17. Effect of WHSV on the catalytic performance of 1-butene epoxidation. The low and high WHSVs are 1.16 and 1.26 g/(g TS-1·h), respectively.

References