

## Supplementary Materials

# Influence of Impurities in a Methanol Solvent on the Epoxidation of Propylene with Hydrogen Peroxide over Titanium Silicalite-1

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**Table S1.** Influence of fusel alcohol content on the product distribution and turnover numbers in epoxidation of propylene with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

| Impurity          | Content, wt. % | TON <sup>b</sup> | Selectivity, %    |                   |                 |                   |                   |                 |                 |                 |
|-------------------|----------------|------------------|-------------------|-------------------|-----------------|-------------------|-------------------|-----------------|-----------------|-----------------|
|                   |                |                  | 1M2P <sup>c</sup> | 2M1P <sup>c</sup> | PG <sup>c</sup> | DGME <sup>c</sup> | PGME <sup>c</sup> | AA <sup>c</sup> | PA <sup>c</sup> | AT <sup>c</sup> |
| none <sup>d</sup> | 0.00           | 314.5            | 0.50              | 0.52              | 0.17            | 0.08              | 0.00              | 0.23            | 0.06            | 0.00            |
| ethanol           | 1.00           | 296.8            | 0.48              | 0.46              | 0.17            | 0.06              | 0.01              | 0.22            | 0.06            | 0.00            |
|                   | 1.50           | 286.8            | 0.45              | 0.45              | 0.15            | 0.05              | 0.02              | 0.26            | 0.06            | 0.01            |
|                   | 2.00           | 282.9            | 0.38              | 0.42              | 0.14            | 0.04              | 0.02              | 0.28            | 0.07            | 0.01            |
|                   | 2.50           | 267.9            | 0.38              | 0.41              | 0.14            | 0.03              | 0.03              | 0.29            | 0.07            | 0.01            |
|                   | 2.50           | 267.9            | 0.38              | 0.41              | 0.14            | 0.03              | 0.03              | 0.29            | 0.07            | 0.01            |
| 2-propanol        | 0.50           | 296.8            | 0.45              | 0.49              | 0.17            | 0.06              | 0.00              | 0.21            | 0.07            | 0.03            |
|                   | 0.75           | 286.8            | 0.43              | 0.47              | 0.15            | 0.06              | 0.00              | 0.22            | 0.07            | 0.05            |
|                   | 1.00           | 282.9            | 0.41              | 0.47              | 0.15            | 0.04              | 0.00              | 0.25            | 0.08            | 0.07            |
|                   | 1.25           | 267.9            | 0.37              | 0.38              | 0.14            | 0.03              | 0.00              | 0.26            | 0.09            | 0.08            |
| 1-propanol        | 0.50           | 297.7            | 0.51              | 0.55              | 0.18            | 0.06              | 0.00              | 0.21            | 0.11            | 0.00            |
|                   | 0.75           | 289.0            | 0.45              | 0.49              | 0.18            | 0.05              | 0.00              | 0.22            | 0.11            | 0.00            |
|                   | 1.00           | 282.5            | 0.44              | 0.49              | 0.17            | 0.05              | 0.00              | 0.24            | 0.14            | 0.01            |
|                   | 1.25           | 266.0            | 0.43              | 0.48              | 0.16            | 0.05              | 0.00              | 0.26            | 0.14            | 0.01            |

Note:

<sup>a</sup> Reaction conditions: pre-adsorbed TS-1 powder 0.4 g, fresh methanol or simulated methanol solvents containing ethanol, 2-propanol and 1-propanol 35.5 mL, H<sub>2</sub>O<sub>2</sub> (50 wt.%) 4.5 mL, NH<sub>3</sub>·H<sub>2</sub>O (0.32 mol/L) 0.2 mL, propylene pressure 0.6 MPa, 50 °C, 1 h.

<sup>b</sup> Turnover number: mol of propylene oxide obtained per mol of titanium present in catalyst.

<sup>c</sup> 1M2P, 2M1P, PG, DGME, PGME, AA, PA and AT were 1-methoxy-2-propanol, 2-methoxy-1-propanol, propylene glycol, dipropylene glycol methyl ether, propylene glycol monoethyl ether, acetaldehyde, propionaldehyde and acetone, respectively.

<sup>d</sup> None represents free of impurities in methanol solvent.

**Table S2.** Influence of ketone and aldehyde content on the product distribution and turnover numbers in epoxidation of propylene with  $\text{H}_2\text{O}_2^{\text{a}}$ 

| Impurity          | Content (ppm) | TON <sup>b</sup> | Selectivity       |                   |                 |                   |
|-------------------|---------------|------------------|-------------------|-------------------|-----------------|-------------------|
|                   |               |                  | 1M2P <sup>c</sup> | 2M1P <sup>c</sup> | PG <sup>c</sup> | DGME <sup>c</sup> |
| none <sup>d</sup> | 0             | 314.5            | 0.50              | 0.52              | 0.17            | 0.08              |
| acetone           | 200           | 305.4            | 0.47              | 0.51              | 0.17            | 0.06              |
|                   | 400           | 287.6            | 0.44              | 0.51              | 0.17            | 0.04              |
|                   | 600           | 257.6            | 0.44              | 0.47              | 0.16            | 0.04              |
|                   | 800           | 201.0            | 0.36              | 0.40              | 0.14            | 0.03              |
| acetaldehyde      | 200           | 314.8            | 0.46              | 0.51              | 0.16            | 0.07              |
|                   | 400           | 315.0            | 0.50              | 0.52              | 0.16            | 0.07              |
|                   | 600           | 318.6            | 0.51              | 0.55              | 0.17            | 0.07              |
|                   | 800           | 319.6            | 0.53              | 0.56              | 0.20            | 0.08              |
| propionaldehyde   | 200           | 315.4            | 0.42              | 0.52              | 0.17            | 0.08              |
|                   | 400           | 312.8            | 0.43              | 0.53              | 0.16            | 0.07              |
|                   | 600           | 311.5            | 0.47              | 0.55              | 0.16            | 0.07              |
|                   | 800           | 307.5            | 0.47              | 0.57              | 0.15            | 0.06              |

Note:

<sup>a</sup> Reaction conditions: methanol containing series of content of ketone and aldehyde (acetone, acetaldehyde and propionaldehyde), other conditions were given in table S1.

<sup>b</sup> Turnover number: seen in table S1.

<sup>c</sup> 1M2P, 2M1P, PG, DGME were seen in table S1.

<sup>d</sup> None represents free of impurities in methanol solvent.

**Table S3.** Influence of ester content on the product distribution and turnover numbers in epoxidation of propylene with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

| Impurity          | Content (ppm) | TON <sup>b</sup> | Selectivity       |                   |                 |                   |
|-------------------|---------------|------------------|-------------------|-------------------|-----------------|-------------------|
|                   |               |                  | 1M2P <sup>c</sup> | 2M1P <sup>c</sup> | PG <sup>c</sup> | DGME <sup>c</sup> |
| none <sup>d</sup> | 0             | 314.5            | 0.50              | 0.52              | 0.17            | 0.08              |
| methyl formate    | 400           | 318.9            | 0.47              | 0.52              | 0.17            | 0.05              |
|                   | 600           | 313.9            | 0.50              | 0.57              | 0.17            | 0.06              |
|                   | 800           | 309.7            | 0.51              | 0.59              | 0.16            | 0.07              |
|                   | 1000          | 307.3            | 0.52              | 0.59              | 0.16            | 0.07              |
|                   | 400           | 293.7            | 0.42              | 0.53              | 0.16            | 0.04              |
| methyl acetate    | 600           | 276.0            | 0.43              | 0.54              | 0.16            | 0.05              |
|                   | 800           | 265.2            | 0.45              | 0.55              | 0.16            | 0.05              |
|                   | 1000          | 263.7            | 0.49              | 0.56              | 0.18            | 0.06              |

Note:

<sup>a</sup> Reaction conditions: methanol containing series of content of ester (methyl formate and methyl acetate), other conditions were given in table S1.

<sup>b</sup> Turnover number: seen in table S1.

<sup>c</sup> 1M2P, 2M1P, PG, DGME were seen in table S1.

<sup>d</sup> None represents free of impurities in methanol solvent.

**Table S4.** Influence of acetal content on the product distribution and turnover numbers in epoxidation of propylene with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

| Impurity             | Content<br>(wt.%) | TON <sup>b</sup> | Selectivity       |                   |                 |                   |
|----------------------|-------------------|------------------|-------------------|-------------------|-----------------|-------------------|
|                      |                   |                  | 1M2P <sup>c</sup> | 2M1P <sup>c</sup> | PG <sup>c</sup> | DGME <sup>c</sup> |
| none <sup>d</sup>    | 0.00              | 314.5            | 0.50              | 0.52              | 0.17            | 0.08              |
| dimethoxymethane     | 0.05              | 313.9            | 0.46              | 0.61              | 0.17            | 0.07              |
|                      | 0.10              | 312.8            | 0.45              | 0.63              | 0.17            | 0.07              |
|                      | 0.15              | 311.8            | 0.43              | 0.66              | 0.18            | 0.05              |
|                      | 0.20              | 311.5            | 0.43              | 0.66              | 0.19            | 0.05              |
|                      | 0.25              | 311.5            | 0.43              | 0.66              | 0.19            | 0.05              |
| 1,1-dimethoxyethane  | 0.05              | 311.8            | 0.47              | 0.54              | 0.17            | 0.07              |
|                      | 0.10              | 308.0            | 0.47              | 0.54              | 0.15            | 0.06              |
|                      | 0.15              | 303.8            | 0.43              | 0.56              | 0.14            | 0.06              |
|                      | 0.20              | 289.1            | 0.41              | 0.67              | 0.13            | 0.05              |
| 1,1-dimethoxypropane | 0.05              | 300.9            | 0.46              | 0.54              | 0.17            | 0.08              |
|                      | 0.10              | 289.5            | 0.44              | 0.56              | 0.17            | 0.05              |
|                      | 0.15              | 286.1            | 0.43              | 0.59              | 0.16            | 0.07              |
|                      | 0.20              | 285.3            | 0.43              | 0.60              | 0.15            | 0.08              |

Note:

<sup>a</sup> Reaction conditions: methanol containing series of content of acetal (dimethoxymethane, 1,1-dimethoxyethane and 1,1-dimethoxypropane), other conditions were given in table S1.

<sup>b</sup> Turnover number: seen in table S1.

<sup>c</sup> 1M2P, 2M1P, PG, DGME were seen in table S1.

<sup>d</sup> None represents free of impurities in methanol solvent.

**Table S5.** Influence of amine content on the product distribution and turnover numbers in epoxidation of propylene with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

| Impurity          | Content (ppm) | TON <sup>b</sup> | Selectivity       |                   |                 |                   |
|-------------------|---------------|------------------|-------------------|-------------------|-----------------|-------------------|
|                   |               |                  | 1M2P <sup>c</sup> | 2M1P <sup>c</sup> | PG <sup>c</sup> | DGME <sup>c</sup> |
| none <sup>d</sup> | 0             | 314.5            | 0.50              | 0.52              | 0.17            | 0.08              |
| methylamine       | 10            | 175.6            | 0.31              | 0.50              | 0.13            | 0.03              |
|                   | 25            | 153.3            | 0.29              | 0.54              | 0.12            | 0.02              |
|                   | 50            | 152.2            | 0.28              | 0.78              | 0.11            | 0.02              |
|                   | 75            | 145.1            | 0.25              | 0.82              | 0.10            | 0.01              |
| ethylamine        | 10            | 175.6            | 0.29              | 0.79              | 0.13            | 0.05              |
|                   | 25            | 153.3            | 0.28              | 0.81              | 0.15            | 0.05              |
|                   | 50            | 152.2            | 0.27              | 1.01              | 0.14            | 0.04              |
|                   | 75            | 145.1            | 0.26              | 1.12              | 0.12            | 0.04              |

<sup>a</sup> Reaction conditions: methanol containing series of content of amines (methylamine and ethylamine) other conditions were given in table S1.

<sup>b</sup> Turnover number: seen in table S1.

<sup>c</sup> 1M2P, 2M1P, PG, DGME were seen in table S1.

<sup>d</sup> None represents free of impurities in methanol solvent.

**Table S6.** Contents of impurities in simulated methanol solvents

| Impurity |                            | Impurities levels in simulated solvents |      |      |      |      |
|----------|----------------------------|-----------------------------------------|------|------|------|------|
| fusel    | ethanol, wt.%              | 0                                       | 1.0  | 1.5  | 2.0  | 2.5  |
| alcohol  |                            |                                         |      |      |      |      |
|          | 2-propanol, wt.%           | 0                                       | 0.5  | 0.75 | 1.0  | 1.25 |
|          | 1-propanol, wt.%           | 0                                       | 0.5  | 0.75 | 1.0  | 1.25 |
| aldehyde | acetaldehyde, ppm          | 0                                       | 200  | 400  | 600  | 800  |
|          | propionaldehyde, ppm       | 0                                       | 200  | 400  | 600  | 800  |
| ketone   | acetone, ppm               | 0                                       | 200  | 400  | 600  | 800  |
| ester    | methyl formate, ppm        | 0                                       | 400  | 600  | 800  | 1000 |
|          | methyl acetate, ppm        | 0                                       | 400  | 600  | 800  | 1000 |
| acetal   | dimethoxymethane, wt.%     | 0                                       | 0.05 | 0.10 | 0.15 | 0.20 |
|          | 1,1-dimethoxyethane, wt.%  | 0                                       | 0.05 | 0.10 | 0.15 | 0.20 |
|          | 1,1-dimethoxypropane, wt.% | 0                                       | 0.05 | 0.10 | 0.15 | 0.20 |
| amine    | methylamine, ppm           | 0                                       | 10   | 25   | 50   | 75   |
|          | ethylamine, ppm            | 0                                       | 10   | 25   | 50   | 75   |