Highly selective skeletal isomerization of cyclohexene over zeolite-based catalysts for high-purity methylcyclopentene production

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### Tables

**Table S1** Gas product yields of catalytic cyclohexene conversion over different catalysts.

| Catalyst          | H₂ yield (wt%) | CH₄ yield (wt%) | C₂ yield (wt%) | C₃ yield (wt%) | C₄ yield (wt%) |
|-------------------|---------------|----------------|---------------|---------------|---------------|
| None              | 0.02          | BDL*           | BDL           | BDL           | BDL           |
| ZSM-5             | 0.21          | 0.03           | 3.55          | 5.58          | 2.72          |
| NaZSM-5           | 0.34          | 0.02           | 5.17          | 3.52          | 0.55          |
| UZSM-5            | 0.26          | BDL            | 1.56          | 0.98          | 1.95          |
| NaUZSM-5          | 0.23          | BDL            | 1.10          | 1.69          | 0.24          |
| Co/NaUZSM-5       | 0.18          | BDL            | 0.26          | 0.11          | 0.15          |
| Silica            | 0.14          | BDL            | 1.66          | 1.31          | 0.29          |
| Alumina           | 0.01          | 0.59           | 2.75          | 0.38          | 0.72          |
| Zirconia          | 0.01          | 0.24           | 0.84          | 0.10          | BDL           |
| Titania           | 0.06          | 0.62           | 0.82          | 0.48          | BDL           |

*BDL: below detection limit*
Table S2 Overall analysis results of catalytic cyclohexene pyrolysis over different catalysts.

| Catalyst       | Cyclohexene conversion (%) | Gas yield (wt%) | Liquid yield (wt%) | Coke yield (wt%) | Overall mass balance (%) |
|----------------|---------------------------|----------------|-------------------|-----------------|--------------------------|
| None           | 7                         | 0.5            | 98.5              | 0               | 99.0                    |
| ZSM-5          | 100                       | 12.3           | 88.5              | 1.3             | 102.1                   |
| NaZSM-5        | 100                       | 10.0           | 88.8              | 1.2             | 100.0                   |
| UZSM-5         | 93                        | 6.0            | 91.2              | 0.9             | 98.1                    |
| NaUZSM-5       | 44                        | 3.3            | 94.8              | 0.4             | 98.5                    |
| Co/NaUZSM-5    | 47                        | 1.5            | 96.8              | 0.4             | 98.8                    |
| Silica         | 35                        | 3.5            | 94.8              | 1.4             | 99.6                    |
| Alumina        | 41                        | 7.0            | 92.6              | 1.3             | 100.9                   |
| Zirconia       | 23                        | 4.0            | 95.0              | 1.2             | 100.2                   |
| Titania        | 45                        | 5.0            | 92.5              | 2.7             | 100.2                   |
| Catalyst            | BET surface area (m² g⁻¹) | Total Pore volume (cm³ g⁻¹) | Micropore surface area (m² g⁻¹) | t-plot Micropore volume (cm³ g⁻¹) |
|---------------------|---------------------------|----------------------------|---------------------------------|---------------------------------|
| ZSM-5               | 395                       | 0.27                       | 222                             | 0.12                            |
| NaZSM-5             | 377                       | 0.25                       | 221                             | 0.12                            |
| UZSM-5              | 318                       | 0.20                       | 241                             | 0.13                            |
| NaUZSM-5            | 319                       | 0.20                       | 235                             | 0.12                            |
| Co/NaUZSM-5         | 327                       | 0.22                       | 192                             | 0.10                            |
| Silica              | 229                       | 0.21                       | 0                               | 0                               |
| Alumina             | 173                       | 0.68                       | 18                              | 0.01                            |
| Zirconia            | 139                       | 0.12                       | 2                               | 0                               |
| Titania             | 18                        | 0.06                       | 0                               | 0                               |
Table S4 Surface acidity of zeolite-based and metal oxide-based catalysts derived from peak integration of NH$_3$-TPD signals.

| Catalyst        | Weak site acidity (mmol g$^{-1}$) | Strong site acidity (mmol g$^{-1}$) | Total acidity (mmol g$^{-1}$) |
|-----------------|-----------------------------------|------------------------------------|-------------------------------|
| ZSM-5           | 232                               | 184                                | 417                           |
| NaZSM-5         | 293                               | 22                                 | 315                           |
| UZSM-5          | 62                                | 0                                  | 62                            |
| NaUZSM-5        | 32                                | 0                                  | 32                            |
| Co/NaUZSM-5     | 8                                 | 16                                 | 24                            |
| Silica          | 15                                | 0                                  | 15                            |
| Alumina         | 47                                | 0                                  | 47                            |
| Zirconia        | 115                               | 13                                 | 128                           |
| Titania         | 45                                | 23                                 | 67                            |
Table S5 Content of several elements in zeolite-based catalysts determined by ICP-OES.

| Catalyst          | Na (wt%) | K (wt%) | Co (wt%) |
|-------------------|----------|---------|----------|
| ZSM-5             | BDL      | BDL     | BDL      |
| NaZSM-5           | 0.32     | 0.003   | BDL      |
| UZSM-5            | BDL      | 1.23**  | BDL      |
| NaUZSM-5          | 1.07     | 0.99    | BDL      |
| Co/NaUZSM-5       | 0.99     | 1.01    | 9.04     |

*BDL: below detection limit

**The presence of K in UZSM-5 and relevant catalysts can be due to high potassium content (0.49 wt%) in template solution TPAOH
Table S6 Unit cell parameters for ZSM-5 and UZSM-5.

| Sample  | a (Å)     | b (Å)     | c (Å)     | Volume (Å³) |
|---------|-----------|-----------|-----------|-------------|
| ZSM-5   | 19.7928   | 19.1059   | 12.8254   | 4850.04     |
| UZSM-5  | 19.6728   | 19.3627   | 13.1278   | 5000.61     |
| Catalyst         | BET surface area (m² g⁻¹) | Total Pore volume (cm³ g⁻¹) | Micropore surface area (m² g⁻¹) | t-plot Micropore volume (cm³ g⁻¹) |
|------------------|----------------------------|----------------------------|---------------------------------|----------------------------------|
| NaUZSM-5         | 319                        | 0.20                       | 235                             | 0.12                             |
| 5Co/NaUZSM-5     | 299                        | 0.22                       | 200                             | 0.11                             |
| 10Co/NaUZSM-5    | 327                        | 0.22                       | 192                             | 0.10                             |
| 15Co/NaUZSM-5    | 270                        | 0.20                       | 146                             | 0.07                             |

Table S7 Structural properties of UZSM-5 catalysts with different Co loadings.
Table S8 Surface acidity of NaUZSM-5 loaded with various metals derived from peak integration of NH$_3$-TPD signals.

| Catalyst         | Weak site acidity (mmol g$^{-1}$) | Strong site acidity (mmol g$^{-1}$) | Total acidity (mmol g$^{-1}$) |
|------------------|-----------------------------------|-------------------------------------|-------------------------------|
| NaUZSM-5         | 32                                | 0                                   | 32                            |
| Co/NaUZSM-5      | 8                                 | 16                                  | 24                            |
| Mo/NaUZSM-5      | 201                               | 0                                   | 201                           |
| Ag/NaUZSM-5      | 16                                | 0                                   | 16                            |
| Ga/NaUZSM-5      | 35                                | 0                                   | 35                            |
| Ce/NaUZSM-5      | 48                                | 0                                   | 48                            |
Table S9 Structural properties of Co/NaUZSM-5 and Co/NaUZSM-5-IPB.

| Catalyst                  | BET Surface area (m² g⁻¹) | Micropore surface area (m² g⁻¹) | External surface area (m² g⁻¹) |
|---------------------------|---------------------------|---------------------------------|--------------------------------|
| Co/NaUZSM-5               | 327                       | 192                             | 135                            |
| Co/NaUZSM-5-IPB           | 305                       | 169                             | 136                            |
**Tables S10** Detailed compositional analysis liquid products over zeolite-based and metal oxide-based catalysts for catalytic cyclohexene pyrolysis. The blank cells indicate the yield of corresponding product is below detection limit.

| Selectivity* (wt%) | ZSM-5 | NaZSM-5 | UZSM-5 | NaUZSM-5 | Co/NaUZSM-5 | Silica | Alumina | Zirconia | Titania |
|-------------------|-------|---------|--------|----------|-------------|--------|---------|----------|--------|
| p                 | 1.02  | 0.84    | 0.53   | 0.74     |              |        |         |          |        |
| 2-mcp             | 8.22  | 10.87   | 10.80  | 7.06     | 10.83       | 9.31   | 10.61   |          |        |
| 3-mcp             | 3.49  | 5.90    | 4.99   | 3.83     | 5.49        | 4.92   | 4.98    |          |        |
| mcpa              | 0.70  | 0.95    | 6.79   | 1.15     | 1.00        | 9.00   | 3.86    | 17.16    | 6.66   |
| 5-m1,3-cpd        |       |         |        |          | 1.16        | 1.12   | 0.48    | 0.98     |        |
| 1-mcp             | 45.85 | 71.74   | 79.41  | 46.8     | 71.01       | 44.90  | 55.73   |          |        |
| b                 | 11.61 | 21.23   | 1.01   | 1.13     | 10.96       | 1.80   | 0.75    | 0.83     |        |
| cha               | 1.09  | 0.66    | 1.65   | 3.49     | 2.24        | 5.16   | 4.97    | 20.79    | 18.38  |
| chde              | 0.83  | 0.46    | 6.68   | 0.91     | 1.02        | 1.09   | 0.48    | 1.15     | 1.10   |
| t                 | 16.27 | 27.32   | 4.37   | 3.64     | 0.55        | 14.98  | 1.08    | 1.01     | 0.73   |
| eb                | 5.08  | 4.65    | 1.79   |          |             |        |         |          |        |
| x                 | 20.55 | 24.46   | 4.51   |          |             |        |         |          |        |
| C9a               | 25.55 | 13.3    | 6.93   |          |             |        |         |          |        |
| C10a              | 5.96  | 3.71    | 6.65   |          |             |        |         |          |        |
| C11a              | 5.57  | 1.68    | 2.07   |          |             |        |         |          |        |
| C12+a             | 5.23  |         |        |          |             |        |         |          |        |

*p=pentene, 2-mp=2-methylpentene, 3-mcp=3-methylcyclopentene, 4-mcp=4-methylcyclopentene, mcpa=methylcyclopentane, 5m-1,3-cpd=5-methyl-1,3-cyclopentadiene, 1-mcp=1-methylcyclopentene, b=benzene, cha=cyclohexane, chde=cyclohexadiene, t=toluene, eb=ethylbenzene, x=xylenes, C9a=C9 aromatics, C10a=C10 aromatics, C11a=C11 aromatics, C12+a=aromatics with 12 or more carbon atoms*
Table S11 Equilibrium calculation of methylocyclopentene isomers.

| Reactant | Product | $\Delta G(673.15 \text{ K, kJ mol}^{-1})$ | ln$K$ | $K$  |
|----------|---------|---------------------------------|-------|------|
| 1-mcp    | 3-mcp   | 8.0                             | -1.44 | 0.237|
| 1-mcp    | 4-mcp   | 16.8                            | -2.99 | 0.050|
**Table S12** Comparison of relative content among methylcyclopentene isomers derived from thermal equilibrium calculation and experimental result.

| Method                        | 1-mcp (%) | 3-mcp (%) | 4-mcp (%) |
|-------------------------------|-----------|-----------|-----------|
| Thermal equilibrium calculation | 77.7      | 18.4      | 3.9       |
| Experimental result           | 79.5      | 14.6      | 5.9       |