The interactive role of methane beyond a reactant in crude oil upgrading

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Supplementary Information

Contents

Fig. S1 N2 adsorption isotherms of fresh and used catalysts with different reaction cycles under methane and nitrogen. .......................................................................................................................................................................................... 3

Fig. S2 NH3-TPD patterns of fresh and used catalysts with different reaction cycles under methane and nitrogen. .......................................................................................................................................................................................... 4

Fig. S3 DTG patterns of used catalysts with different reaction cycles under methane and nitrogen. ......... 5

Fig. S4 Optimized structures of nitrogen adsorption on the external surface and in the internal pore structure of the zeolitic catalysts through DFT calculation. Energy unit: kJ mol\(^{-1}\). .......................................................................................... 6

Fig. S5 Optimized structures of n-butylbenzene (nBuB) adsorption on the external surface and in the internal pore structure of the zeolitic catalysts through DFT calculation. (a) ZSM-5 catalyst, (b) Mo/ZSM-5, (c) Ce/ZSM-5. Energy unit: kJ mol\(^{-1}\). .................................................................................................................... 7

Fig. S6 The typical profiles of (a) temperature and (b) pressure during the catalytic heavy oil upgrading process.......................................................................................................................................................................................... 8

Fig. S7 The typical profiles of (a) temperature and (b) pressure during the catalytic n-butylbenzene conversion process.................................................................................................................................................................................. 9
Fig. S8 Other conformations of methane adsorption inside and outside the zeolitic pore structure. Energy unit: kJ mol$^{-1}$

Fig. S9 Other conformations of $n$-butylbenzene (nBuB) adsorption inside and outside the zeolitic pore structure. Energy unit: kJ mol$^{-1}$

Table S1 Properties of crude oil and liquid products after the upgrading process over MOU catalyst under methane and nitrogen.

Table S2 Overall analysis results of $n$-butylbenzene reactions over catalysts with different reaction cycles.

Table S3 Gas analysis of $n$-butylbenzene reactions over catalysts with different reaction cycles.

Table S4 Overall analysis results of $n$-butylbenzene reactions over regenerated catalysts.

Table S5 Gas analysis of $n$-butylbenzene reactions over regenerated catalysts.

Table S6 Calculation of the $n$-butylbenzene (nBuB) adsorption over ZSM-5 with and without dispersion corrections.

Table S7 Additional physical and compositional properties of the crude oil.

Table S8 Contents of several typical metal impurities in crude oil and liquid products after the upgrading process.
**Fig. S1** N₂ adsorption isotherms of fresh and used catalysts with different reaction cycles under methane and nitrogen.
**Fig. S2** NH$_3$-TPD patterns of fresh and used catalysts with different reaction cycles under methane and nitrogen.
Fig. S3 DTG patterns of used catalysts with different reaction cycles under methane and nitrogen.
**Fig. S4** Optimized structures of nitrogen adsorption on the external surface and in the internal pore structure of the zeolitic catalysts through DFT calculation. Energy unit: kJ mol$^{-1}$. 

$E_{\text{ads}}(\text{N}_2) = -16.0$  $E_{\text{ads}}(\text{N}_2) = -17.5$
**Fig. S5** Optimized structures of \textit{n}-butylbenzene (nBuB) adsorption on the external surface and in the internal pore structure of the zeolitic catalysts through DFT calculation. (a) ZSM-5 catalyst, (b) Mo/ZSM-5, (c) Ce/ZSM-5. Energy unit: kJ mol\textsuperscript{-1}.

\[ E_{\text{ads}}(\text{nBuB}) = \begin{array}{c}
-112.0 \\
-121.6 \\
-146.1 \\
-262.9 \\
-321.8 \\
-380.0 \\
\end{array} \]
Fig. S6 The typical profiles of (a) temperature and (b) pressure during the catalytic heavy oil upgrading process.
**Fig. S7** The typical profiles of (a) temperature and (b) pressure during the catalytic $n$-butylbenzene conversion process.
**Fig. S8** Other conformations of methane adsorption inside and outside the zeolitic pore structure. Energy unit: kJ mol$^{-1}$
Other conformations of \(n\)-butylbenzene (nBuB) adsorption inside and outside the zeolitic pore structure. Energy unit: kJ mol\(^{-1}\)
**Table S1** Properties of crude oil and liquid products after the upgrading process over MOU catalyst under methane and nitrogen.

| Property                      | Property |  |              |  |  |  |              |  |  |  |  |
|-------------------------------|----------|  |  |  |  |  |  |  |  |  |  |
|                               | Crude oil| Manchester | Prod-M1 | Prod-M1 | Prod-M1 | Prod-N1 | Prod-N1 | Prod-N1 | Prod-N1 | Prod-N1 | Prod-N1 |
| Overall mass balance (%)      |          | Repeat 1 | Repeat 2 | Repeat 3 |          | Repeat 1 | Repeat 2 | Repeat 3 |          | Repeat 1 | Repeat 2 | Repeat 3 | Repeat 3 |
| Gas yield (wt%)               |          |         |         |         |          |         |         |         |          |         |         |         |         |
| Liquid yield (wt%)            |          |         |         |         |          |         |         |         |          |         |         |         |         |
| Coke yield (wt%)              |          |         |         |         |          |         |         |         |          |         |         |         |         |
| Liquid viscosity (mPa s)      |          |         |         |         |          |         |         |         |          |         |         |         |         |
| Liquid density (g cm⁻³)       |          |         |         |         |          |         |         |         |          |         |         |         |         |
|                               |          | 99.5    | 99.9    | 99.9    | 99.9    | 99.7    | 99.7    | 99.1    |          |         |         |         |         |
|                               |          | 2.2     | 2.4     | 2.3     | 1.9     | 2.1     | 2.5     |          |          |         |         |         |         |
|                               |          | 97.1    | 97.3    | 97.3    | 97.8    | 97.4    | 96.4    |          |          |         |         |         |         |
|                               |          | 0.23    | 0.23    | 0.24    | 0.24    | 0.22    | 0.22    |          |          |         |         |         |         |
|                               |          | 3373    | 105     | 102     | 105     | 151     | 147     | 150     |          |         |         |         |         |
|                               |          | 0.96570 | 0.94455 | 0.94520 | 0.94520 | 0.95167 | 0.95160 | 0.95170 |          |         |         |         |         |


Table S2 Overall analysis results of *n*-butylbenzene reactions over catalysts with different reaction cycles.

| Entry     | Butylbenzene conversion (%) | Gas yield (wt%) | Liquid yield (wt%) | Coke yield (wt%) | Overall mass balance (%) |
|-----------|------------------------------|-----------------|-------------------|-----------------|--------------------------|
| MOU       | 96±1                         | 5±0.5           | 92±5              | 1.0±0.1         | 98±5                     |
| Cat-M1    | 50±1                         | 2±0.2           | 97±5              | 0.8±0.1         | 100±5                    |
| Cat-N1    | 43±1                         | 2±0.2           | 97±5              | 0.8±0.1         | 100±5                    |
| Cat-M2    | 41±1                         | 2±0.2           | 95±5              | 0.7±0.1         | 98±5                     |
| Cat-N2    | 34±1                         | 1±0.2           | 97±5              | 0.7±0.1         | 99±5                     |
| Cat-M3    | 36±1                         | 1±0.2           | 95±5              | 0.6±0.1         | 97±5                     |
| Cat-N3    | 23±1                         | 1±0.2           | 96±5              | 0.5±0.1         | 98±5                     |
| SiC       | 21±1                         | 1±0.2           | 95±5              | 0.0±0.1         | 96±5                     |

*All yields are based on *n*-butylbenzene feedstock.*
Table S3 Gas analysis of \( n \)-butylbenzene reactions over catalysts with different reaction cycles.

| Entry  | CH\(_4\) conversion (wt\%) | H\(_2\) yield (wt\%)\(^\dagger\) | C\(_2\) yield (wt\%) | C\(_3\) yield (wt\%) | C\(_4\) yield (wt\%) |
|--------|-----------------------------|----------------------------------|----------------------|----------------------|----------------------|
| MOU    | 2.1±1.0                     | 0.10±0.02                        | 0.34±0.07            | 1.7±0.3              | 2.6±0.5              |
| Cat-M1 | 1.3±1.0                     | 0.05±0.01                        | 0.80±0.16            | 0.20±0.04            | 0.78±0.11            |
| Cat-N1 | 1.6±1.0                     | 0.05±0.01                        | 1.07±0.21            | 0.28±0.06            | 0.66±0.13            |
| Cat-M2 | 1.4±1.0                     | 0.04±0.01                        | 0.90±0.18            | 0.12±0.02            | 0.72±0.14            |
| Cat-N2 | 1.3±1.0                     | 0.04±0.01                        | 0.86±0.17            | 0.1±0.02             | 0.38±0.05            |
| Cat-M3 | 1.1±1.0                     | 0.03±0.01                        | 0.96±0.20            | 0.08±0.02            | 0.31±0.06            |
| Cat-N3 | 1.1±1.0                     | 0.03±0.01                        | 0.94±0.19            | 0.08±0.02            | 0.24±0.04            |
| SiC    | 0.4±1.0                     | 0.01±0.005                       | 0.69±0.14            | 0.05±0.01            | 0.32±0.06            |

\(^\dagger\)All yields are based on \( n \)-butylbenzene feedstock.
**Table S4** Overall analysis results of *n*-butylbenzene reactions over regenerated catalysts.

| Entry   | Butylbenzene conversion (%) | Gas yield (wt%) | Liquid yield (wt%) | Coke yield (wt%) | Overall mass balance (%) |
|---------|-----------------------------|-----------------|-------------------|------------------|--------------------------|
| Cat-M1-R | 93±1                        | 4±5             | 95±5              | 0.9±0.1          | 100±5                    |
| Cat-N1-R | 93±1                        | 5±5             | 92±5              | 0.9±0.1          | 98±5                     |

*All yields are based on *n*-butylbenzene feedstock.*
Table S5 Gas analysis of \(n\)-butylbenzene reactions over regenerated catalysts.

| Entry   | \(\text{CH}_4\) conversion (wt\%) | \(\text{H}_2\) yield (wt\%)\(^*\) | \(\text{C}_2\) yield (wt\%) | \(\text{C}_3\) yield (wt\%) | \(\text{C}_4\) yield (wt\%) |
|---------|-----------------------------------|-----------------------------------|----------------------------|----------------------------|----------------------------|
| Cat-M1-R | 1.9±1.0                           | 0.06±0.01                         | 0.17±0.03                  | 1.6±0.3                    | 2.3±0.3                    |
| Cat-N1-R | 2.4±1.0                           | 0.07±0.02                         | 0.16±0.03                  | 1.7±0.3                    | 2.5±0.5                    |

\(^*\)All yields are based on \(n\)-butylbenzene feedstock.
Table S6 Calculation of the *n*-butylbenzene (nBuB) adsorption over ZSM-5 with and without dispersion corrections.

| Dispersion Correction | ZSM-5 (a.u.) | nBuB (a.u.) | In/Out | ZSM-5-nBuB (a.u.) | Adsorption Energy (kJ mol⁻¹) |
|-----------------------|--------------|-------------|--------|-------------------|----------------------------|
| No                    | -41680.239   | -385.844    | In     | -42066.184        | -262.9                     |
| No                    | -41680.239   | -385.844    | Out    | -42066.126        | -112.0                     |
| Yes                   | -41680.787   | -385.910    | In     | -42066.804        | -279.8                     |
| Yes                   | -41680.787   | -385.910    | Out    | -42066.751        | -141.9                     |
**Table S7** Additional physical and compositional properties of the crude oil.

| Property                          | Crude oil |
|----------------------------------|-----------|
| API gravity                      | 15.0      |
| Characterization K factor        | 9.3       |
| Classification                   | Aromatic  |
| TAN (mg KOH g⁻¹)                 | 1.06      |
| Asphaltene content (wt%)         | 17.7      |
| Olefin content (wt%)             | BDL*      |
| Carbon content (wt%)             | 85.07     |
| Hydrogen content (wt%)           | 11.44     |
| H:C ratio                        | 1.61      |
| Oxygen content (wt%)             | 0.57      |
| Nitrogen content (wt%)           | 0.21      |
| Sulfur content (wt%)             | 3.06      |
| Ca (ppm)                         | 49        |
| V (ppm)                          | 125       |
| Ni (ppm)                         | 63        |

*BDL: below detection limit*
Table S8 Contents of several typical metal impurities in crude oil and liquid products after the upgrading process.

| Oil sample | Ca (ppm) | V (ppm) | Ni (ppm) |
|------------|----------|---------|----------|
| Crude oil  | 49       | 125     | 63       |
| Prod-M1    | 50       | 126     | 60       |
| Prod-N1    | 50       | 128     | 61       |
| Prod-M2    | 48       | 124     | 60       |
| Prod-N2    | 50       | 128     | 58       |
| Prod-M3    | 49       | 129     | 61       |
| Prod-N3    | 51       | 130     | 60       |