# Supplementary Information

# Catalytic Methane Dissociation and its Non-oxidative Coupling in Metal-Dispersed Molten Salt Media: An *Ab Initio* Molecular Dynamics Investigation

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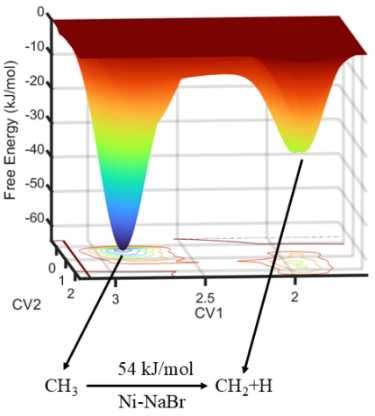
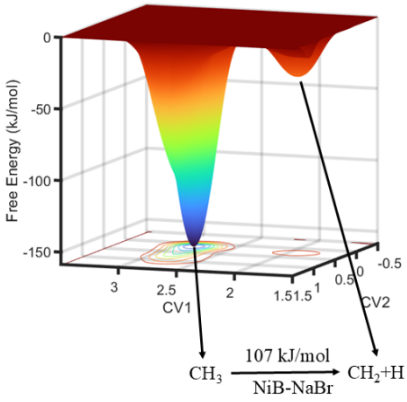
## S1. Metadynamics calculated free energy surfaces for sequential dehydrogenation of CHx (x = 3, 2, 1) and C-C coupling reactions at 1200 K in Ni-NaBr, NiB-NaBr, Cu-NaBr, and CuB-NaBr systems.

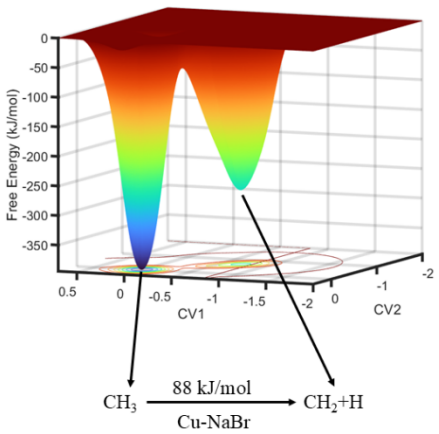
We have performed metadynamics simulations in conjunction with CPMD to obtain the free energy landscapes of all reactions. To perform metadynamics simulation at 1200 K two CVs are chosen for each of these reactions and these CVs are explained in detail in Table 1. The free energy barriers for all the reactions were determined from the free energy diagrams and mentioned in the following figures.



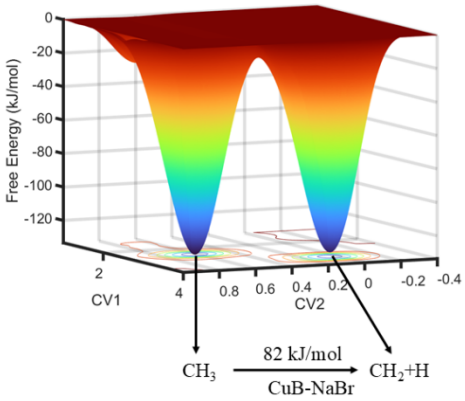

(a)




(b)




(c)




(d)

**Figure S1**. Metadynamics calculated free energy (1200 K) reaction profile for the $CH_3$ dehydrogenation to $CH_2$ in (a) Ni-NaBr, (b) NiB-NaBr, (c) Cu-NaBr, and (d) CuB-NaBr are shown. The free energy barrier (kJ/mol) is shown above the arrow. Refer to Table 1 for the definition of collective variables CV1 and CV2.

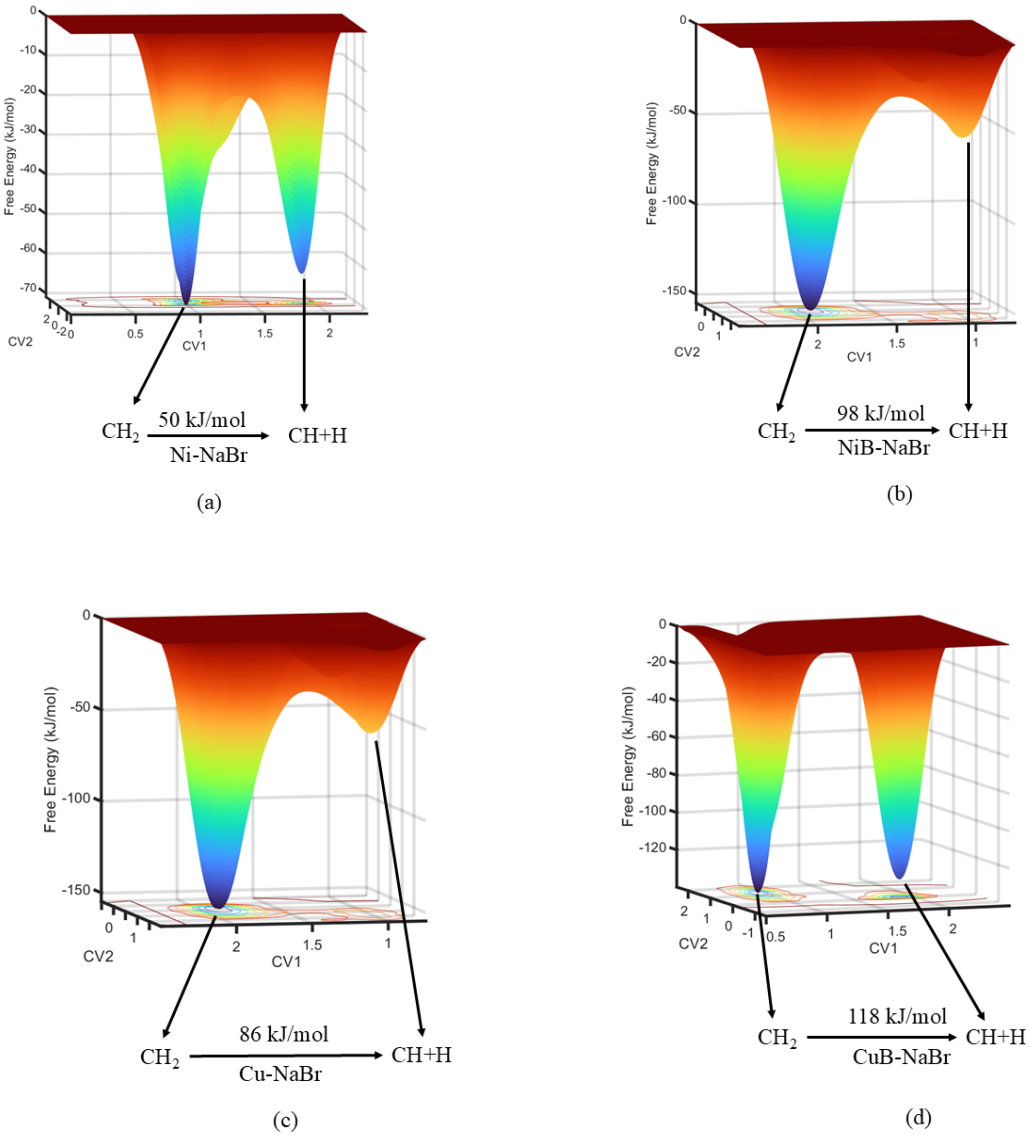



**Figure S2**. Metadynamics calculated free energy (1200 K) reaction profile for the $CH_2$ dehydrogenation to CH in (a) Ni-NaBr, (b) NiB-NaBr, (c) Cu-NaBr, and (d) CuB-NaBr are shown. The free energy barrier (kJ/mol) is shown above the arrow. Refer to Table 1 for the definition of collective variables CV1 and CV2.

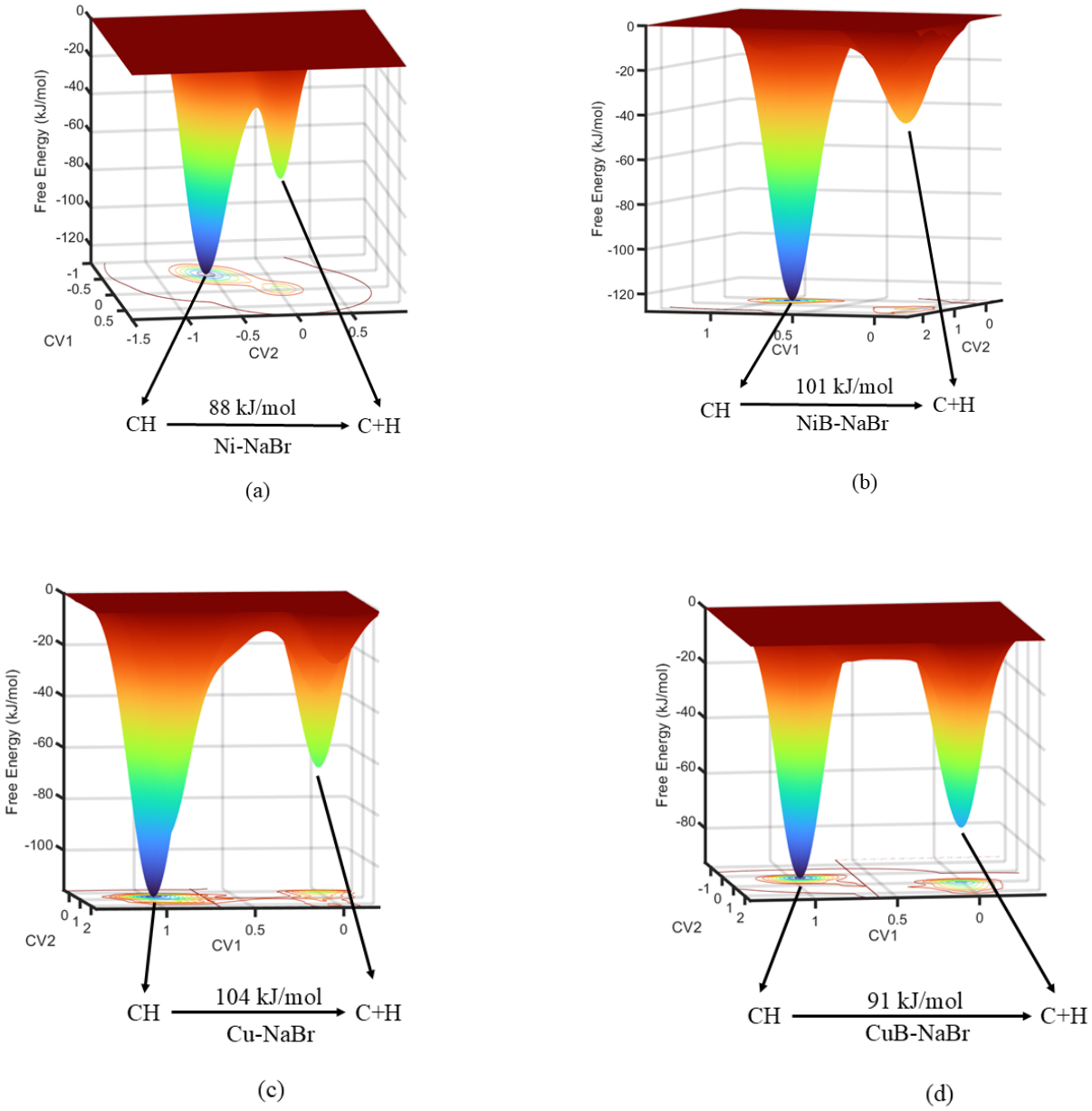



**Figure S3**. Metadynamics calculated free energy (1200 K) reaction profile for the CH dehydrogenation to C in (a) Ni-NaBr, (b) NiB-NaBr, (c) Cu-NaBr, and (d) CuB-NaBr are shown. The free energy barrier (kJ/mol) is shown above the arrow. Refer to Table 1 for the definition of collective variables CV1 and CV2.

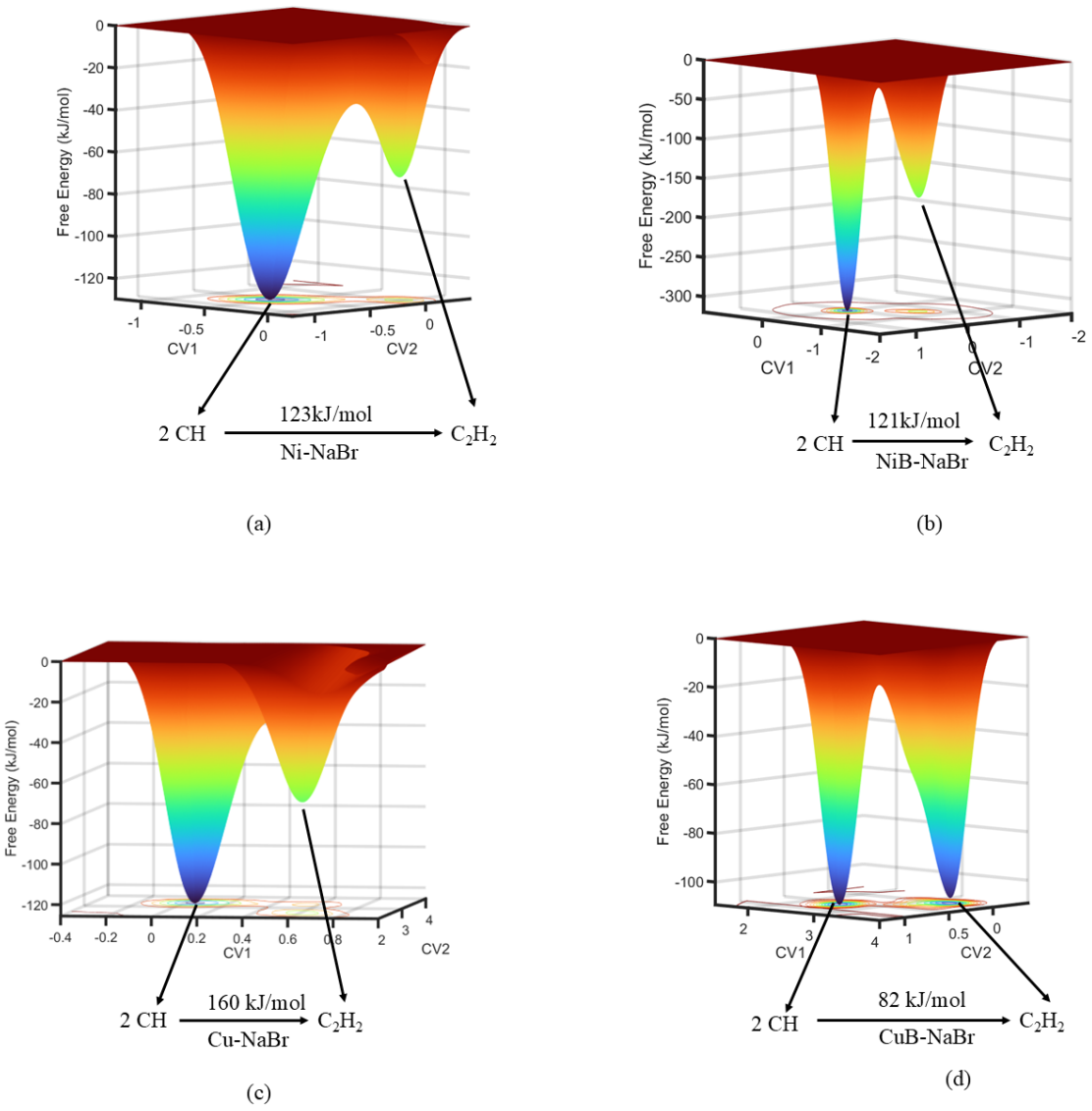



**Figure S4**. Metadynamics calculated free energy (1200 K) reaction profile for the CH-CH coupling reaction in (a) Ni-NaBr, (b) NiB-NaBr, (c) Cu-NaBr, and (d) CuB-NaBr are shown. The free energy barrier (kJ/mol) is shown above the arrow. Refer to Table 1 for the definition of collective variables CV1 and CV2.

## S2. Car – Parrinello Molecular Dynamics and Metadynamics Sample Input File

Sample input file for the CPMD – metadynamics simulation for the first dehydrogenation reaction in the Ni-NaBr system.

```
*******************************************************************************

&CPMD
 MOLECULAR DYNAMICS CP
 RESTART WAVEFUNCTION COORDINATES VELOCITIES NOSEE NOSEP NOSEC
 TRAJECTORY SAMPLE XYZ
  10
 NOSE IONS
    1200.0d0   3500.0d0
 NOSE ELECTRONS
    0.18  10000.0d0
 MAXSTEP
  5000
 TIMESTEP
  4.0
 EMASS
  200.0
 VDW CORRECTION
 LSD
 MEMORY BIG
&END
&VDW
 EMPIRICAL CORRECTION
 VDW PARAMETERS
  ALL DFT-D2
 S6GRIMME
  PBE
 END EMPIRICAL CORRECTION
&END

&SYSTEM
 SYMMETRY
  4
 ANGSTROM
 CELL ABSOLUTE DEGREE
  9.93626 9.93626 40.0 90.0 90.0 120.0
 DUAL
  4.0
 CUTOFF
  80.0
 CHARGE
  0
&END
```

```
&DFT
 FUNCTIONAL PBE
 GC-CUTOFF
 1.0d-06
&END
&ATOMS
*Ni_MT_PBE_NLCC.psp KLEINMAN-BYLANDER NLCC
 LMAX=D LOC=P
  64
-0.36    6.21    0.86
-2.34    8.82    5.3
0.28     4.51    4.81
5.2      8.96    6.18
8.96     2.25    4.78
7.86     4.38    5.34
2.85     8.81    5.19
0.17     8.76    5.11
1.58     6.59    4.86
1.13     2.54    6.19
3.87     2.17    5.8
3.81     6.63    6.08
5.15     4.4     5.76
6.37     6.55    5.58
6.31     2.29    5.68
-0.93    6.52    5.07
-0.84    7.86    7.47
5.34     1.53    8.22
2.67     5.9     8.36
6.61     7.78    7.74
8        1.26    7.41
4.28     7.86    8.4
5.51     5.64    8.2
1.26     3.84    8.62
1.6      7.85    7.47
10.26    1.62    8.49
8.11     5.7     8.09
0.54     5.62    6.97
6.71     3.58    7.9
2.74     1.46    7.94
2.71     4.44    6.23
3.61     1.12    3.21
3.64     5.29    3.89
-1.48    8.51    0.84
0.84     4.17    0.02
5.84     4.09    0.86
2.09     6.39    0.7
4.53     6.25    1.62
3.14     4.3     1.49
6.72     6.37    0.69
1.96     1.95    1.24
4.65     2.04    1.38
9.47     1.85    0.05
3.52     8.24    0.28
7.19     1.88    0.82
5.66     8.45    1.42
```

0.98 8.48 0.94
8.38 4.1 0.51
-0.13 7.48 3.02
8.65 5.31 2.85
7.36 7.59 3.39
6.35 1.06 3.29
4.83 7.63 3.77
8.63 0.89 2.71
2.38 7.48 2.85
10.88 1.15 3.93
1.35 5.28 2.77
9.94 3.03 2.36
5.1 3.3 3.43
7.41 3.32 3.02
6.16 5.41 3.3
2.42 3.14 3.79
3.82 3.7 8.17
9.1 3.56 7.28

*Na_MT_PBE_SEMI.psp KLEINMAN-BYLANDER
LMAX=P LOC=S
35
-21.1 10.74 21.09
-24.77 12.27 29.38
3.76 5.35 38.79
-8.17 11.32 17.78
-0.46 -6.68 38.58
2.24 2.11 13.65
10.26 6.12 9.83
3.4 -5.91 15.29
-0.91 -1.28 31.67
6.94 -3.26 13.17
-3.53 6.73 17.64
5.22 14.13 37.66
-14.21 7.37 25.75
-15.46 9.93 21.35
-16.23 1.27 32.51
11.11 -5.05 10.89
-8.43 14 20.42
-20.75 9.81 28.96
9.98 -0.91 15.24
-3.72 -5.32 17.13
-11.59 16.14 19.05
-4.55 15.93 21.85
11.32 0.66 10.41
-0.58 3.51 24.5
-2.07 1.81 36.36
10.16 8.78 14.5
10.75 0.15 38.06
-3.51 8.1 28.52
-7.17 -3.35 32.43
-4.12 14.7 26.71
-8.24 -1.34 23.5
-8.17 7.61 34.6
1.25 -3.19 35.58

```
-11.68   11.58    25.23
7.07     0.37     10.71

*Br_MT_PBE.psp KLEINMAN-BYLANDER
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  35
-8.22    9.89     21.33
-17.84   0.01     30.72
1.63     2.56     38.02
-15.26   5.76     22
-4.34    -0.27    32.17
5.39     -4.49    14.55
12.23    -2.15    10.41
4.25     1.45     10.47
-14.05   10.9     27.04
8.17     8.05     16.34
-10.56   1.4      34.12
-4.94    5.16     33.14
-1.21    4.52     17.33
-21.81   8.91     24.74
-12.29   4.28     37.27
11.32    3.93     11.21
-5.02    10.1     18.85
-6.78    5.29     26.55
1.98     -0.69    13.16
-2.62    8.44     21.12
-7.38    11.44    28.56
-16.11   8.81     23.81
7.05     1.66     13.12
-3.75    11.8     21.5
8.26     7.63     38.55
2.18     8.77     16.11
7.09     0.21     38.15
-5.86    5.6      29.32
-6.17    -1.85    34.7
-7.42    13.31    22.91
-10.58   -3.55    18.31
3.57     6.87     35.94
-6.96    -2.49    28.46
-0.94    12.57    14.79
0.47     7.12     12.21

*C_MT_PBE.psp KLEINMAN-BYLANDER
 LMAX=P LOC=P
  1
4.28     4.43     10.96

*H_MT_PBE.psp KLEINMAN-BYLANDER
 LMAX=S LOC=S
  4
3.93     4.66     11.97
3.53     4.73     10.23
4.46     3.35     10.87
5.22     4.97     10.77
```

```
CONSTRAINTS
FIX STRUCTURE SHOVE
1
DIST 135 64 8 -1
END CONSTRAINTS

METADYNAMICS COLLECTIVE VARIABLES

DEFINE VARIABLES
2
COOR_RF INDAT 135 3 6 6 1.8 SCF 1.0 KCV 1.0 MCV 150
26 64 24
DIFCOOR INDAT 135 26 4 6 6 1.5 SCF 1.0 KCV 1.0 MCV 150
136 137 138 139
END DEFINE

LAGRANGE TEMPERATURE
1200.0
LAGRANGE TEMPCONTROL
1200.0 200.0
HILLS = 0.1 0.001
METASTEPNUM
5000
MOVEMENT CHECK
0.02
MINSTEPNUM INTERMETA
100
CHECK DELAY
10
METASTORE NO TRAJECTORY
20 1 100000 MONITOR
10
END METADYNAMICS
&END

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```

## S3. Variation of fictitious electronic kinetic energy vs time during the equilibration (without thermostats) of the first dehydrogenation reaction.

We have monitored the variation of fictitious electronic kinetic energy during the equilibration run to see if there is any deviation from the BO surface.

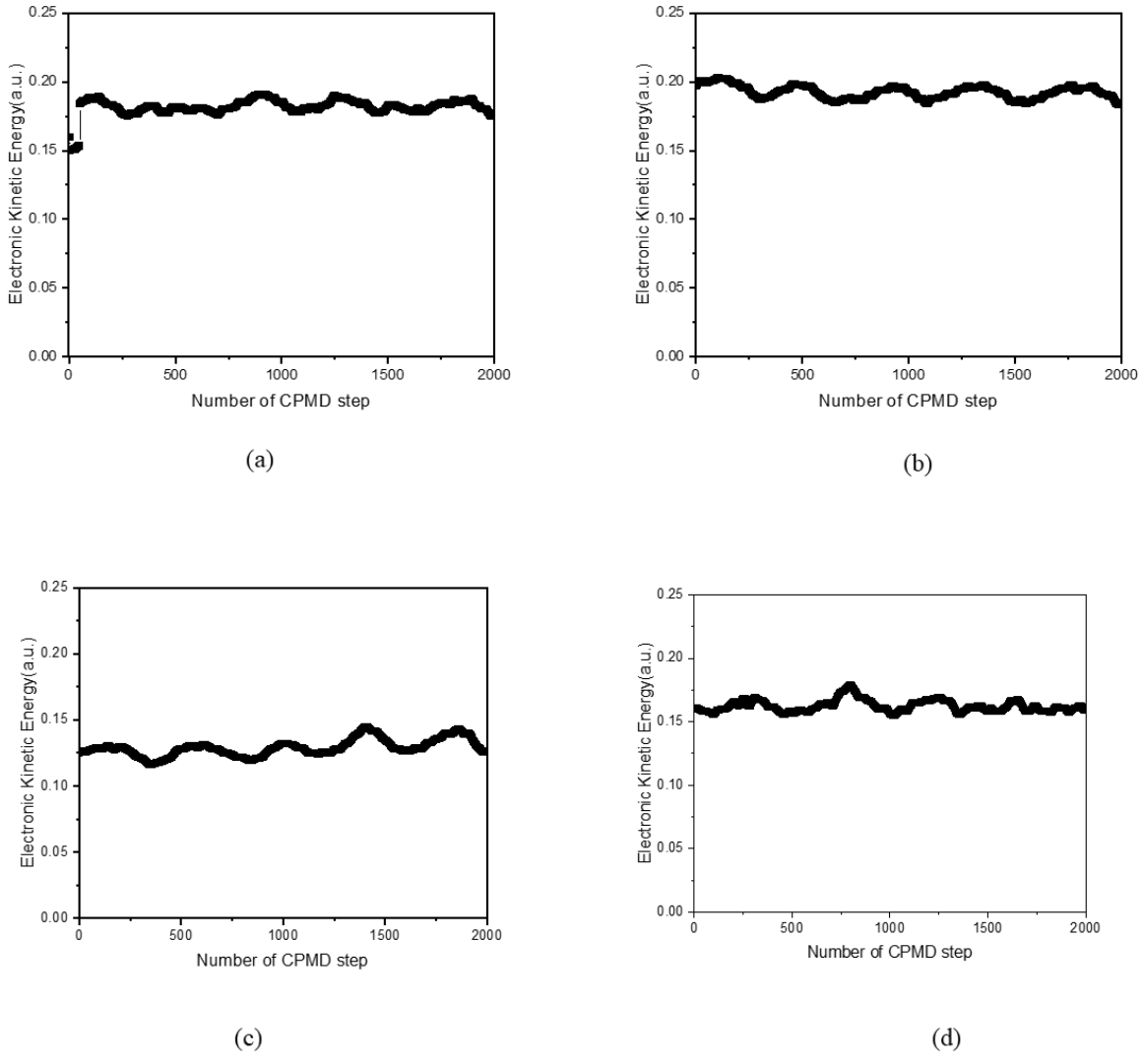


**Figure S5**. Plot of fictitious electronic kinetic energy vs time during the equilibration of the first dehydrogenation reaction a) Ni-NaBr, b) NiB-NaBr, c) Cu-NaBr, d) CuB-NaBr system.

## S4. Computational parameter optimization

**Table S1**. Optimisation of K-Points for all four systems.

| Molten Media | The difference in total energy (kJ/mol) of the system between K=2×2×1 and K=1×1×1 sampling |
|---|---|
| Ni-NaBr | 3.38 |
| NiB-NaBr | 4.53 |
| Cu-NaBr | 3.18 |
| CuB-NaBr | 4.92 |

We performed the DFT calculation with a k-points sampling of 2×2×1 with the Monkhorst-pack scheme for all systems. These calculations showed that the total energy difference between the 2×2×1 k-points and the Gamma point is small (< 5 kJ/mol) across all four systems studied. We also note that the computational cost of employing a 2×2×1 Monkhorst-pack k-point grid is approximately four times higher than that of the Gamma point calculation. Given the negligible difference in energy, and considering that Gamma-point calculations are significantly less computationally demanding we justify the use of Gamma-point sampling in our CPMD simulations.

## S5. Variations of distance over time between the carbon atom and the top Cu layer for (a) Cu-NaBr and (b) CuB-NaBr medium

In this section, we report the variation in the distance between the carbon atom and the top Cu layer during the simulation period. We observed carbon diffusion from the top surface into the Cu bulk at approximately 2.5 ps in the Cu-NaBr medium, whereas no such migration from the top surface into the Cu bulk was observed in the CuB-NaBr medium.

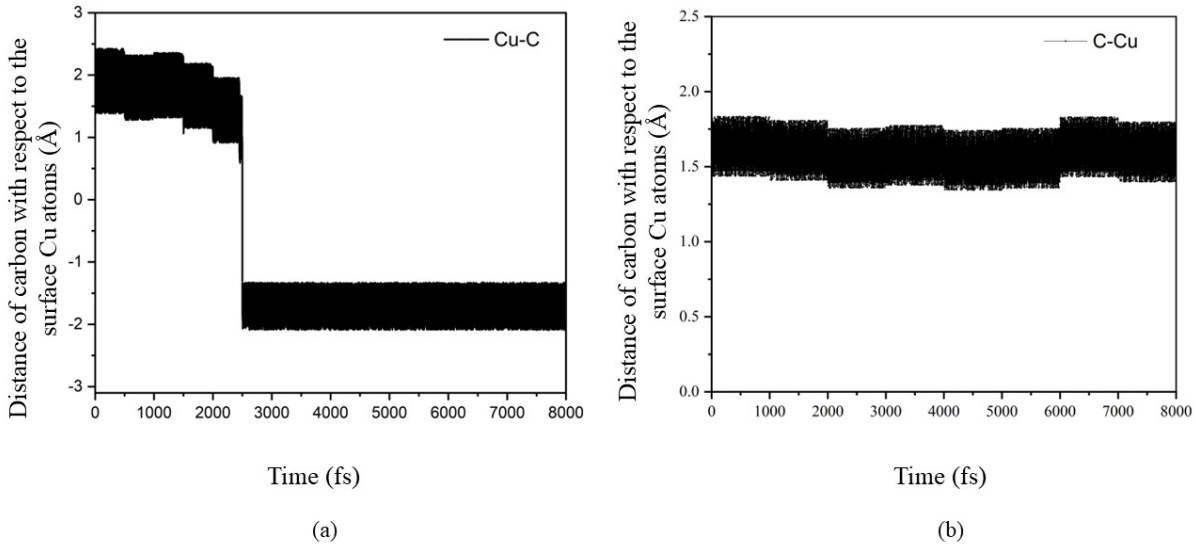


**Figure S6.** Figure 6. Time trajectory of the distance between the carbon atom and the surface Cu atoms during CPMD simulation for (a) Cu-NaBr and (b) CuB-NaBr system.

## S6. Comparison of free energy barriers of the current study and the reported values in the literature.

**R1:** $CH_4 \rightarrow CH_3^* + H^*$
**R2:** $CH_3^* \rightarrow CH_2^* + H^*$
**R3:** $CH_2^* \rightarrow CH^* + H^*$
**R4:** $CH^* \rightarrow C^* + H^*$
**R5:** $CH_2^* + CH_2^* \rightarrow C_2H_4^*$
**R6:** $CH^* + CH^* \rightarrow C_2H_2^*$

**Table S2a**. Free energy barriers of all reactions for sequential dehydrogenation of $CH_4$ and the C-C coupling reactions in all molten mediums. Activation barriers that are reported at ground state in literature are marked as green.

| Reaction | Activation barrier (kJ/mol) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ni-NaBr | Ni | NiB-NaBr | NiB | Cu-NaBr | Cu | CuB-NaBr | CuB |
| | Present work | Reported | Present work | Reported | Present work | Reported | Present work | Reported |
| R1 | 151 | 164[1],129[2] | 112 | 107[1] | 91 | 90[3] | 86 | 75[5] |
| R2 | 54 | 58[1] | 107 | 87[1] | 88 | 132[4] | 82 | 120[5] |
| R3 | 50 | 35[1] | 98 | 56[1] | 86 | 91[4] | 118 | 161[5] |
| R4 | 88 | 126[1] | 101 | 96[1] | 104 | 178[4] | 91 | 197[5] |
| R5 | 208 | - | 190 | - | 182 | - | 109 | 92[5] |
| R6 | 123 | - | 121 | - | 160 | - | 82 | - |

**Table S2b.** C-H distances and C-C distances in the Transition state on Ni-NaBr, NiB-NaBr, Cu-NaBr, CuB-NaBr mediums. All distances are given Å. All reactions are mentioned above.

| Reaction | Ni-NaBr | | NiB-NaBr | | Cu-NaBr | | CuB-NaBr | |
|---|---|---|---|---|---|---|---|---|
| | $d_{C-H}$ | $d_{C-C}$ | $d_{C-H}$ | $d_{C-C}$ | $d_{C-H}$ | $d_{C-C}$ | $d_{C-H}$ | $d_{C-C}$ |
| R1 | 1.83 | - | 1.81 | - | 1.78 | - | 1.77 | - |
| R2 | 1.69 | - | 1.76 | - | 1.74 | - | 1.70 | - |
| R3 | 1.68 | - | 1.74 | - | 1.73 | - | 1.80 | - |
| R4 | 1.72 | - | 1.79 | - | 1.81 | - | 1.78 | - |
| R5 | - | 2.00 | - | 2.01 | - | 2.04 | - | 2.06 |
| R6 | - | 2.06 | - | 2.07 | - | 2.09 | - | 2.12 |

References

1) Mohan, O., Lapkin, A. A., & Mushrif, S. H. 2020, Catal. Sci. Technol., 10(19), 6628-6643.

2) D. W. Blaylock, Y. A. Zhu and W. H. Green, Top. Catal., 2011, 54, 828–844

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4) Gajewski, G., & Pao, C. W. 2011, J. Chem. Phys., 135(6).

5) Q. T. Trinh, A. Banerjee, Y. Yang and S. H. Mushrif, J. Phys. Chem. C, 2017, 121, 1099–1112.