Supplementary Information (SI)

Thermal and structural studies of carbon coated Mo$_2$C synthesized via in-situ single step reduction-carburization

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Appendix S 1

\[ \text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \text{Mo} + \text{Mo}_2\text{C} \quad (\text{S 1.1}) \]

\[ \text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \text{Mo}_2\text{C} \quad (\text{S 1.2}) \]

Firstly, reduction of MoO$_3$ to MoO$_2$ followed by MoO$_2$ to Mo$_2$C. The reduction of MoO$_2$ to Mo$_2$C can occur through an intermediate product of metallic Mo as shown in equation S1.1. Sometimes reaction proceeds without formation of metallic phase depending on reaction conditions as given in equation S1.2 and is more favorable for endothermic solid state reactions.

Scherrer formula

The crystallite size obtained from Scherrer equation is volume weighted quantity and uses full width at half maxima for determination of crystallite size, $D$ [38]:

\[ D = \frac{k \lambda}{\beta \cos \theta} \Rightarrow \cos \theta = \frac{k \lambda}{D} \left( \frac{1}{\beta} \right) \quad (\text{S 1.3}) \]

Where, $k$ is shape factor, $\lambda$ is wavelength of X-ray radiation, $D$ is effective crystallite size in nanometers, $\beta$ is peak width corrected for instrumental broadening as described in equation (1) and $\theta$ is Bragg angle.

Williamson Hall analysis

Stokes and Wilson assigned a mathematical relation for peak broadening solely due to strain [1]. Crystal imperfection and distortion constitute the strain broadening and the induced strain is given as follows:
As Scherrer equation follows $1/\cos \theta$ dependency, the Williamson-Hall method varies with $\tan \theta$ and allows the separation of diffracted beams when both crystallite size and strain are simultaneously involved [38]. Even though $\beta$ is combination of equation (S1.3) and (S1.4), Williamson Hall plot is used to separate the individual effects:

$$\beta \cos \theta = \left[ \frac{k \lambda}{D} \right] + [4 \varepsilon \sin \theta]$$  \hspace{1cm} (S 1.5)

Equation (S1.5) represents the uniform deformation model where strain was considered to be isotropic through whole crystal.

In many cases the strain homogeneity assumption and isotropy is not fulfilled, so uniform stress deformation model and uniform deformation energy density model come into consideration.

The anisotropic nature of Young’s modulus is considered by both the models, hence are more realistic routes [2, 39]. In uniform deformation stress model, anisotropic micro strain $\varepsilon$ is exhibited due to isotropic stress $\sigma$. The linear proportionality between stress and strain is given by Hook’s law, $\sigma = \varepsilon E_{hkl}$. Considering this, Williamson-Hall equation has been formulated as:

$$\beta = \left( \frac{k \lambda}{D} \right) + \left( \frac{4 \sigma \sin \theta}{E_{hkl}} \right)$$  \hspace{1cm} (S 1.6)

Where $E_{hkl}$ is Young modulus and for hexagonal crystal phases, it can be calculated by following relation: [5]

$$E_{hkl} = \left( h^2 + \frac{(h+2k)^2}{3} + \frac{(a_t}{c})^2 \right) \times \left[ S_{11} \left( h^2 + \frac{(h+2k)^2}{3} \right) + S_{33} \left( \frac{a_t}{c} \right)^2 \right] + \left( 2S_{13} + S_{44} \right) \left( h^2 + \frac{(h+2k)^2}{3} \right) \left( \frac{a_t}{c} \right)^2 \right]^{-1}$$  \hspace{1cm} (S 1.7)
Where $S_{11}$, $S_{13}$, $S_{33}$ and $S_{44}$ are elastic compliances of Mo$_2$C having values of $2.4 \times 10^{-3}$, $-0.68 \times 10^{-3}$, $2.56 \times 10^{-3}$ and $7.353 \times 10^{-3}$ GPa$^{-1}$ respectively [3-4]. Young modulus was calculated as 390.49 GPa which is in close approximation to earlier reported by [5]. Plotting $(4 \sin \theta /E_{hkl})$ on x-axis and $(\beta \cos \theta)$ on y-axis as shown in Fig. S2.a, the value of stress was calculated from slope of fitted line and crystallite size is extracted from intercept reported in Table A2. The uniform deformation energy density model assumes isotropic energy density as a cause of anisotropic deformation within the crystal. The energy density $u$ as a function of strain for a system that follows Hook’s law is given by $u = e^2 E_{hkl}/2$. According to energy and strain relation, the uniform deformation energy model is given by following mathematical relation:

$$\beta = \left( \frac{k_d}{D} \right) + \left( 4 \sin \theta \left( \frac{2u}{E_{hkl}} \right)^{\frac{1}{2}} \right)$$

Plots were drawn with $4 \sin \theta \left( \frac{2u}{E_{hkl}} \right)^{\frac{1}{2}}$ and $\beta \cos \theta$ on x-axis and y-axis respectively and data fitted to lines as shown in (Fig. S2.b). The slope of the fitted line is used to estimate the value of energy density $u$ while as crystallite size $D$ is estimated from intercept as given in Table A2. The deformation stress and deformation energy density are related as $u = \sigma^2 /E_{hkl}$.

At constant temperature, with increase in synthesis time R-4 (2h), R-5 (5h), R-3 (10h) and R-6 (12h), the strain value increases up to 10h while, the value decreases when synthesis time is increased up to 12h where the carbon drain out from the system and the product is converted back to MoO$_2$, showing the reversibility of the reaction.
Table S 1. Williamson Hall analysis Mo$_2$C phase obtained samples.

| Sample ID | USDM | USEDLM | USDML | USEDM | USDML | USEDM | USDML |
|-----------|------|--------|-------|-------|--------|-------|--------|
|           | D (nm) | $\sigma$ (GPa) | $\varepsilon \times 10^{-4}$ | D (nm) | $\sigma$ (GPa) | $\varepsilon \times 10^{-4}$ | $U \times 10^2$ (KJm$^{-3}$) |
| R-2       | 54.37  | 0.2654  | 6.82  | 56.36 | 0.2876  | 7.38  | 1.06   |
| R-3       | 45.76  | 0.2059  | 5.29  | 46.68 | 0.2182  | 5.60  | 0.61   |
| R-4       | 37.88  | 0.1563  | 4.01  | 38.09 | 0.1612  | 4.13  | 0.33   |
| R-5       | 51.74  | 0.1433  | 3.68  | 51.74 | 0.1580  | 4.05  | 0.32   |
| R-6       | 96.28  | 0.1662  | 6.00  | 96.287| 0.1676 | 4.30  | 0.36   |
Fig. S 1 Rietveld refinement plot and W-H analysis of (R-3 sample). (a) The measured and calculated data are observed by dots and solid curve respectively. The plot below shows the difference between measured and calculated data, whereas the tick marks indicate the bragg positions. (b) Gaussian fitted data, (c) Sherrer plot of sample, (d) UDM, (e) USDM and (f) USEDM model, the crystalline size is extracted from y-intercept of fit, strain and deformation energy density id is estimated from slope of fit.
**Appendix S 2**

**Table S 2.** Various reaction mechanisms involved in a thermal decomposition process.

| Reaction Mechanism | Integral form $g(\alpha)$ |
|--------------------|---------------------------|
| **Diffusion mechanism** | |
| $D_1$ (1 – D diffusion) | $\alpha^2$ |
| $D_2$ (2 – D diffusion) | $\alpha + (1 - \alpha) \ln(1 - \alpha)$ |
| $D_3$ (3 – D diffusion) | $(1 - (1 - \alpha)^{1/3})^2$ |
| $D_4$ (Ginstling-Brounshtein) | $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ |
| **Random nucleation mechanism** | |
| $F_1$ (First order) | $-\ln(1 - \alpha)$ |
| $F_2$ (Second order) | $1/(1 - \alpha)$ |
| $F_3$ (Third order) | $1/2(1 - \alpha)$ |
| **Nucleation and growth mechanism** | |
| $A_2$ (Avrami-Erofeyev) | $(-\ln(1 - \alpha))^{1/2}$ |
| $A_3$ (Avrami-Erofeyev) | $(-\ln(1 - \alpha))^{1/3}$ |
| $A_4$ (Avrami-Erofeyev) | $(-\ln(1 - \alpha))^{1/4}$ |
| **Phase boundary controlled reaction mechanism** | |
| $R_1$ (1-D movement) | $\alpha$ |
| $R_2$ (contracting area) | $1 - (1 - \alpha)^{1/2}$ |
| $R_3$ (contracting volume) | $1 - (1 - \alpha)^{1/3}$ |
Fig. S 2.1 Linear fitted curves of stage 2 corresponding to (a) Diffusion mechanism (b) Random nucleation mechanism (c) Nucleation and growth mechanism and (d) Phase boundary controlled reaction mechanism.
Fig. S 2.2 Linear fitted curves of stage 3 corresponding to (a) Diffusion mechanism (b) Random nucleation mechanism (c) Nucleation and growth mechanism and (d) Phase boundary controlled reaction mechanism.
**Fig. S 2.3** Linear fitted curves of stage 4 corresponding to (a) Diffusion mechanism (b) Random nucleation mechanism (c) Nucleation and growth mechanism and (d) Phase boundary controlled reaction mechanism.
Fig. S 2.4 Linear fitted curves of stage 5 corresponding to (a) Diffusion mechanism (b) Random nucleation mechanism (c) Nucleation and growth mechanism and (d) Phase boundary controlled reaction mechanism.
**Fig. S 2.5** Linear fitted curves of stage 6 corresponding to (a) Diffusion mechanism (b) Random nucleation mechanism (c) Nucleation and growth mechanism and (d) Phase boundary controlled reaction mechanism.
The log-normal probability distribution function is given by following equation:

\[
f(d) = \frac{1}{\sqrt{2\pi \log \sigma_s}} \exp \left\{ -\frac{(\log d - \log \mu_s)^2}{2(\log \sigma_s)^2} \right\} \tag{S 3.1}
\]

Where, \( \log \sigma_s = \sqrt{\frac{\sum (\log d_i - \log \mu_s)^2}{\sum n_i}} \) \tag{S 3.2}

\( \log \mu_s = \frac{\sum d_i}{\sum n_i} \) \tag{S 3.3}

Where, \( f(d) \) signifies the log-normal distribution, \( d_i \) particle diameter, \( n_i \) is the number of particles, \( \mu_s \) is the mean diameter and \( \sigma_s \) is the standard deviation respectively.

Fig. S 3 FESEM micrograph of Mo₂C nanopowder R-3 sample showing spherical/faceted morphology.
Fig. S 3.1 Particle size distribution from TEM using log-normal probability distribution function.
Fig. S 3.2 XPS spectrum of R-6 sample (a) full survey (b) Mo3d (c) C1s and (d) O1s spectrum
Fig S 3.3 Nitrogen adsorption/desorption isotherm of R-3 and R-6 samples
Appendix S 4

\[ \Delta H = \Delta H_{298} + \int_{298}^{T} C_p \, dt \]  

(S 4.1)

\[ C_p = a + b10^{-3}T + C10^{6}T^{-2} + d10^{-6}T^{2} \]  

(S 4.2)

4MoO₃ + Mg → Mo₄O₁₁ + MgO   \hspace{1cm}  (S 4.3)
4MoO₃ + 1/2H₂ + 1/2Mg → Mo₄O₁₁ + 1/2MgO + 1/2 H₂O \hspace{1cm} (S 4.4)
4MoO₃ + 1/2C + 1/2Mg → Mo₄O₁₁ + 1/2MgO + ½CO \hspace{1cm} (S 4.5)
4MoO₃ + 1/2CO + 1/2Mg → Mo₄O₁₁ + 1/2MgO + 1/2CO₂ \hspace{1cm} (S 4.6)
4MoO₃ + 1/16C₂H₆ + 11/16Mg → Mo₄O₁₁ + 11/16MgO + 1/8CO + 3/16H₂O \hspace{1cm} (S 4.7)
4MoO₃ + 1/8C₂H₄ + 1/2Mg → Mo₄O₁₁ + 1/2MgO + 1/4CO + 1/4H₂O \hspace{1cm} (S 4.8)
4MoO₃ + 1/4CH₄ + 1/4Mg → Mo₄O₁₁ + 1/4MgO + 1/4CO + 1/2H₂O \hspace{1cm} (S 4.9)
4MoO₃ + 1/9C₃H₆ + 3/9Mg → Mo₄O₁₁ + 3/9MgO + 1/3CO + 3/9H₂O \hspace{1cm} (S 4.10)
4MoO₃ + 1/9C₃H₈ + 2/9Mg → Mo₄O₁₁ + 2/9MgO + 1/3CO + 8/18H₂O \hspace{1cm} (S 4.11)

**Fig. S 4** Variation in heat of formation with temperature for reduction of MoO₃ to Mo₄O₁₁. It also shows feasibility with both Mg+ H and Mg+ C. However, the reduction of Mg+H (23) and Mg+C (24) is almost similar as the data points overlap. The variation of \( \Delta H \) with temperature of above reactions is shown in Fig. S4.
Appendix S 5

Mo₄O₁₁ + MoO₃ + 11C → 2Mo₂C + 1/2 MoO₂ + 1/2 Mo + 4CO₂ + 5CO  
(S 5.1)
Mo₄O₁₁ + MoO₃ + 6C + 5H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 4CO₂ + 5H₂O  
(S 5.2)
Mo₄O₁₁ + MoO₃ + 8C +7H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 6CO + 7H₂O  
(S 5.3)
Mo₄O₁₁ + MoO₃ + 8C +4H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 3CO + 4H₂O + 3CO₂  
(S 5.4)
Mo₄O₁₁ + MoO₃ + 9C +4H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 4CO + 3H₂O + 3CO₂ +  
H₂  
Mo₄O₁₁ + MoO₃ + 9C +4H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 3CO + 4H₂O + 3CO₂ + C  
(S 5.6)
Mo₄O₁₁ + MoO₃ + 9C +6H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 3CO + 4H₂O + 3CO₂ +  
CH₄  
Mo₄O₁₁ + MoO₃ + 8CO +9H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 9H₂O + 6CO₂  
(S 5.8)
Mo₄O₁₁ + MoO₃ + 6CO +13H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 2CO + 13H₂O +  
2CO₂  
Mo₄O₁₁ + MoO₃ + 9CO +15H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 3CO + 13H₂O +  
3CO₂+ CH₄  
MoO₃ + Mo₄O₁₁ + 5CH₄ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 7H₂O + 3CO₂ + 3H₂  
(S 5.11)
MoO₃ + Mo₄O₁₁ + 7CH₄ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 5H₂O + 2CO + 3CO₂ + 9H₂  
(S 5.12)
MoO₃ + Mo₄O₁₁ + 8CH₄ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 8H₂O + 5CO + CH₄+ 6H₂  
(S 5.13)
MoO₃ + Mo₄O₁₁ + 4CH₄ + H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 2CO₂ + 9H₂O  
(S 5.14)
MoO₃ + Mo₄O₁₁ + 4CH₄ + 2H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + CO₂ + CO+ 10H₂O  
(S 5.15)
MoO₃ + Mo₄O₁₁ + 5CH₄ + 2H₂ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + CO₂ + CO+ 10H₂O +  
CH₄  
MoO₃ + Mo₄O₁₁ + 5C₂H₄ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 2CO₂ + 9H₂O + 6C + H₂  
(S 5.17)
MoO₃ + Mo₄O₁₁ + 4C₂H₄ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 3CO₂ + 4H₂O + 3CO +  
4H₂  
MoO₃ + Mo₄O₁₁ + 3C₂H₆ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 4CO₂ + 5H₂O + 4H₂  
(S 5.19)
MoO₃ + Mo₄O₁₁ + 3C₂H₆ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 2CO + 2CO₂ + 7H₂O +  
2H₂  
MoO₃ + Mo₄O₁₁ + 4C₂H₆ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 2CO + 3CO₂ + 5H₂O +  
CH₄ + 5H₂  
MoO₃ + Mo₄O₁₁ + 3C₃H₆ → 2Mo₂C + 1/2MoO₂ + 1/2Mo + 4CO + 3CO₂ + 3H₂O + 6H₂  
(S 5.22)
MoO\textsubscript{3} + Mo\textsubscript{4}O\textsubscript{11} + 3C\textsubscript{3}H\textsubscript{6} → 2Mo\textsubscript{2}C + 1/2MoO\textsubscript{2} + 1/2Mo + 2CO + 3CO\textsubscript{2} + 5H\textsubscript{2}O + 

(S 5.23)

2CH\textsubscript{4}

MoO\textsubscript{3} + Mo\textsubscript{4}O\textsubscript{11} + 3C\textsubscript{3}H\textsubscript{6} → 2Mo\textsubscript{2}C + 1/2MoO\textsubscript{2} + 1/2Mo + 2CO + 2CO\textsubscript{2} + 7H\textsubscript{2}O + 

(S 5.24)

3C + 2H\textsubscript{2}

**Fig. S 5** Variation with in heat of formation with temperature for reduction-carburization of MoO\textsubscript{3}+Mo\textsubscript{4}O\textsubscript{11} to Mo\textsubscript{2}C, MoO\textsubscript{2} and Mo.
Appendix S 5.A

\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad \Delta H = +172.5 \text{KJ/mol}, \quad \Delta G = -16.2 \text{KJ/mol} \quad (\text{S 5A.1}) \]

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad \Delta H = +131.3 \text{KJ/mol}, \quad \Delta G = -12.3 \text{KJ/mol} \quad (\text{S5A.2}) \]

\[ \text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2 \quad \Delta H = -226.7 \text{KJ/mol}, \quad \Delta G = -163.7 \text{KJ/mol} \quad (\text{S 5A.3}) \]

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2 \quad \Delta H = +134.9 \text{KJ/mol}, \quad \Delta G = -17.65 \text{KJ/mol} \quad (\text{S 5A.4}) \]

\[ 6\text{CH}_4 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_2 + 2\text{CO} + 10\text{H}_2 \quad \Delta H = +681.3 \text{KJ/mol}, \quad \Delta G = -157.1 \text{KJ/mol} \quad (\text{S 5A.5}) \]

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H = +260.76 \text{KJ/mol}, \quad \Delta G = -43.08 \text{KJ/mol} \quad (\text{S 5A.6}) \]

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H = -802 \text{KJmol}^{-1}, \quad \Delta G = -796.8 \text{KJmol}^{-1} \quad (\text{S 5A.7}) \]

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H = -74.8 \text{KJmol}^{-1}, \quad \Delta G = +11.9 \text{KJmol}^{-1} \quad (\text{S 5A.8}) \]

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -250.1 \text{KJmol}^{-1}, \quad \Delta G = +107.8 \text{KJmol}^{-1} \quad (\text{S 5A.9}) \]
Appendix S 6

\[
\begin{align*}
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + 4\text{H}_2 & \rightarrow 5\text{MoO}_2 + 4\text{H}_2\text{O} \quad (S \ 6.1) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + \text{Mg} + 3\text{H}_2 & \rightarrow 5\text{MoO}_2 + 3\text{H}_2\text{O} + \text{MgO} \quad (S \ 6.2) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + 3\text{CO} + 4\text{H}_2 & \rightarrow 5\text{MoO}_2 + 3\text{CO} + 4\text{H}_2\text{O} \quad (S \ 6.3) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + 2\text{CO} + 2\text{H}_2 & \rightarrow 5\text{MoO}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (S \ 6.4) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + \text{CH}_4 & \rightarrow 5\text{MoO}_2 + 2\text{CO}_2 + \text{H}_2\text{O} \quad (S \ 6.5) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + \text{CH}_4 + \text{H}_2 & \rightarrow 5\text{MoO}_2 + \text{CO}_2 + 2\text{H}_2\text{O} + \text{H}_2 \quad (S \ 6.6) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + \text{C}_2\text{H}_4 & \rightarrow 5\text{MoO}_2 + 2\text{CO}_2 + 2\text{H}_2 \quad (S \ 6.7) \\
\text{MoO}_3 + \text{Mo}_4\text{O}_{11} + \text{C}_2\text{H}_4 & \rightarrow 5\text{MoO}_2 + 2\text{CO} + 2\text{H}_2\text{O} \quad (S \ 6.8)
\end{align*}
\]

**Fig. S 6** Variation with in heat of formation with temperature for reduction of MoO3+Mo4O11 to MoO2.
Appendix S 7

MoO₃ + Mo₄O₁₁ +7H₂ + 6C → 5/2Mo₂C + 3.5CO₂ + 7H₂O  
(S 7.1)

MoO₃ + Mo₄O₁₁ + 9H₂ + 10C → 5/2Mo₂C + 6CO + 1/2CH₄ + 8H₂O + C  
(S 7.2)

MoO₃ + Mo₄O₁₁ + 6CH₄ → 5/2Mo₂C + 5/2CO₂ + 9H₂O + 3H₂ + C  
(S 7.3)

MoO₃ + Mo₄O₁₁ + 6CH₄ → 5/2Mo₂C + 5/2CO₂ + 9H₂O + CH₄ + H₂  
(S 7.4)

MoO₃ + Mo₄O₁₁ + 8CH₄ + H₂ → 5/2Mo₂C + 1/2CO₂ + 10H₂O + 3CO + 2CH₄ + 3H₂  
(S 7.5)

MoO₃ + Mo₄O₁₁ + 6CH₄ + H₂ → 5/2Mo₂C + 1/2CO₂ + 11H₂O + 2CO + C + 2H₂  
(S 7.6)

MoO₃ + Mo₄O₁₁ + 5C₂H₄ → 5/2Mo₂C + 3/2CO₂ + 7H₂O + 4C + 4H₂+2CO₂  
(S 7.7)

MoO₃ + Mo₄O₁₁ + 4C₂H₆ → 5/2Mo₂C + 3/2CO₂ + 9H₂O + 2CO + 3H₂+ 2C  
(S 7.8)

MoO₃ + Mo₄O₁₁ + 5C₂H₄ → 5/2Mo₂C + 3/2CO₂ + 6H₂O + 5CO + CH₄ +2H₂  
(S 7.9)

MoO₃ + Mo₄O₁₁ + 3C₃H₆ → 5/2Mo₂C + 1/2CO₂ + 6H₂O + 5CO + 3H₂+ CO₂  
(S 7.10)

Fig. S 7 Variation with in heat of formation with temperature for reduction of MoO₃ + Mo₄O₁₁ to MoO₂ calculated for above reactions at different temperatures up to 800 °C (1073K).
Appendix S 8

Kinetic Theory

The rate of solid state thermal decomposition of chemical reaction can be written as [6]:

\[
\frac{d\alpha}{dt} = kf(\alpha) \tag{S 8.1}
\]

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_f}
\]

where \(n\) is the order of reaction, \(\alpha\) is the degree of conversion, \(m_o\) is the initial mass, \(m_t\) is the mass at time \(t\), \(m_f\) is the final mass and \(k\) is the rate constant which can be expressed by Arreheinus equation:

\[
k = Ae^{-\frac{E_a}{RT}} \tag{S 8.2}
\]

where, \(A\) is the pre-exponential factor, \(E_a\) is the activation energy, \(R\) is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)) and \(T\) is the absolute temperature. The final equation for rate of thermal decomposition process can be expressed as:

\[
\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}}f(\alpha) \tag{S 8.3}
\]

If the temperature increases in a dynamic TG experiment at linear heating rate \(\beta = \frac{dT}{dt}\), the above equation can be written as:

\[
\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} e^{-\frac{E_a}{RT}} \, dT = g(\alpha) \tag{S 8.4}
\]

where, \(g(\alpha)\) is the integral function of degree of conversion. This equation serves as a base for various kinetic methods used to determine thermal kinetic parameters.
Coats-Redfern method

This method is extensively used to determine the reaction mechanism involved in the thermal decomposition of the sample [28]. Coats and Redfern method is an integral method based on Eq. (4) and can be expressed as:

\[
ln \left( \frac{g(\alpha)}{T^2} \right) = ln \left( \frac{AR}{\beta E_a} \right) - \frac{E_a}{RT}
\]  

(S 8.5)

A plot between \(ln \left( \frac{g(\alpha)}{T^2} \right)\) and \(\frac{1000}{T}\) provides information regarding the kinetic parameters of a reaction. The activation energy \((E_a)\) is determined from the slope, whereas the value of pre-exponential factor \((A)\) is calculated from the intercept. However, it is essential to calculate the accurate value of \(g(\alpha)\) which can only be obtained by employing various reaction mechanism involved in a thermal decomposition process, as listed in Table S1 [7]. The choice of exact \(g(\alpha)\) depends on the value of correlation factor \((R^2)\).

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