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Supporting Information:

Crossover of limiting processes in mechanochemical reactions with flow driven by applied mechanical stress

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S1. Derivation

S1.1 Interface model of mechanochemical reaction

Our theory treats the molecular dynamics at the interface between solid particles of reactant A and B. The chemical reaction $\mathrm{A}+\mathrm{B}\rightarrow\mathrm{AB}$ occurs at the interface and produces a phase rich in products there due to the instability arising from the miscibility of products from reactant solids. The time evolution function of the thickness $h(t)$ of the product-rich phase has the form

$$\frac{d}{dt}h(t)=\frac{S(t)}{1-\psi_{\mathrm{A1}}-\psi_{\mathrm{B1}}}-v(t) \tag{S1}$$

with

$$v(t)=\frac{8}{3}\frac{\sigma_{\perp}}{\eta_{\mathrm{AB}}r_0^2}h^3(t). \tag{S2}$$

The reactant solids are assumed as rigid bodies and the product-rich phase is assumed as a liquid due to the small volume of solvent added to the system. $S(t)$ is the reaction rate and $v(t)$ is the speed with which the thickness $h(t)$ of the product-rich phase decreases due to the material flow driven by applied mechanical stress $\sigma_{\perp}$. r_0 is the radius of the interface. η_{AB} is viscosity of the product-rich phase. ψ_{A1} and ψ_{B1} are the volume fraction of reactant A and B at the interface between the product-rich phase and reactant B-rich solid.

The time evolution of the thickness of the system due to the material flow has the form

$$\frac{d}{dt}L(t)=-v(t). \tag{S3}$$

We solve eq. (S3) with the initial condition, $L(0)=L_0$.

The reaction rates in the diffusion-limited, reaction-limited, and marginal regimes have the forms

$$S_{\mathrm{d}}(t)=D_B\frac{\psi_{\mathrm{B1}}^{\mathrm{d}}}{h(t)}, \tag{S4}$$

$$\frac{d}{dt}S_{\mathrm{r}}(t)=\frac{k(\psi_{\mathrm{A1}}^{\mathrm{r}}\psi_{B1}^{\mathrm{r}}-\psi_{\mathrm{A2}}^{\mathrm{r}}\psi_{B2}^{\mathrm{r}})}{1-\psi_{\mathrm{A1}}^{\mathrm{r}}-\psi_{\mathrm{B1}}^{\mathrm{r}}}S(t), \tag{S5}$$

$$\frac{d}{dt}S_{\mathrm{m}}(t) = \frac{k\psi_{\mathrm{A1}}^{\mathrm{r}}\psi_{\mathrm{B1}}^{\mathrm{r}}}{1-\psi_{\mathrm{A1}}^{\mathrm{r}}-\psi_{\mathrm{B1}}^{\mathrm{r}}}S(t), \tag{S6}$$

respectively, where the regimes are indicted by the subscripts `d' (diffusion-limited), `r' (reaction-limited), and `m' (marginal). The limiting process is determined by the minimum among these reaction rates.

The reaction starts from the marginal regime for $L_0 > \lambda_{\mathrm{d}}$ and the reaction-limited regime for $L_0 < \lambda_{\mathrm{d}}$, where $\lambda_{\mathrm{d}}(=\sqrt{D_{\mathrm{B}}/k})$ is the diffusion length. The initial condition of eq. (S5) is

$$S_r(0) = k\psi_{\mathrm{A2}}^{\mathrm{r}}\psi_{\mathrm{B2}}^{\mathrm{r}}L_0 \tag{S7}$$

for $L_0 < \lambda_{\mathrm{d}}$. For $\lambda_{\mathrm{d}} < L_0(< L_2^*)$, where there is a crossover between the marginal to reaction-limited regimes. In this case, the condition

$$h(t) = L(t) - \lambda_d \tag{S8}$$

is imposed to eq. (S1) and (S3) at the crossover. The initial condition of eq. (S6) is

$$S_{\mathrm{m}}(0) = k\psi_{\mathrm{A2}}^{\mathrm{r}}\psi_{\mathrm{B2}}^{\mathrm{r}}\lambda_{\mathrm{d}}. \tag{S9}$$

These initial conditions, eqs. (S7) – (S9), are derived by using eqs. (10) and (13) in the main article for $h(0) = 0$ and $V_{\mathrm{ex}}(0) = 0$. The reaction rate and thickness of the product-rich phase are continuous at the crossovers.

S1.2. Reaction rate and regime diagram without applied mechanical stress

S.1.2.1 Marginal/diffusion-limited crossover

In the marginal regime, the reaction rate is derived by using eq. (S6) as

$$S_{\mathrm{m}}(t) = k\psi_{\mathrm{A2}}^{\mathrm{r}}\psi_{\mathrm{B2}}^{\mathrm{r}}\lambda_{\mathrm{d}}e^{\frac{t}{\tau_{\mathrm{p}}}} \tag{S10}$$

by imposing initial condition, eq. (S9). The thickness of the product-rich phase is derived by solving eq. (S1) with eq. (S10) and $v = 0$ as

$$h_{\mathrm{m}}(t) = \alpha\lambda_{\mathrm{d}}\left(\mathrm{e}^{\frac{t}{\tau_{\mathrm{p}}}} - 1\right). \tag{S11}$$

The thickness of the product-rich phase at the crossover between the marginal and diffusion-limited regime has the form

$$h_{\mathrm{md0}} = \alpha\lambda_{\mathrm{d}}\left(\sqrt{\frac{1}{4}+\frac{\beta}{\alpha^2}}-\frac{1}{2}\right), \tag{S12}$$

which is derived by the continuity of the reaction rate and the thickness of the product-rich phase at the crossover, see eqs. (S4), (S10), and (S11). The time t_{md0} at the marginal/diffusion-limited crossover is derived by using the relationship, $h(t_{\mathrm{md0}}) = h_{\mathrm{md0}}$, as

$$t_{\mathrm{md0}} = \tau_{\mathrm{p}}\ \log\left(\frac{1}{2}+\sqrt{\frac{1}{4}+\frac{\beta}{\alpha^2}}\right), \tag{S13}$$

see eqs. (S11) and (S12).

In the diffusion-limited regime, the thickness of the product-rich phase at the crossover is derived by solving eq. (S1) with eq. (S4) and $v(t) = 0$ as

$$h_{\mathrm{d}}(t) = \sqrt{h_{\mathrm{md0}}^2 + \frac{2\beta\lambda_{\mathrm{d}}^2(t-t_{\mathrm{md0}})}{\tau_{\mathrm{p}}}}, \tag{S14}$$

where we used the continuity of the thickness $h(t)$ at the crossover, $h_{\mathrm{d}}(t_{\mathrm{md0}}) = h_{\mathrm{md0}}$. The reaction rate $S_{\mathrm{d}}(t)$ in the diffusion-limited regime is derived by substituting eq. (S14) into eq. (S4) as

$$S_{\mathrm{d}}(t) = D_{\mathrm{B}}\frac{\psi_{\mathrm{B1}}^{\mathrm{d}}}{\sqrt{h_{\mathrm{md0}}^2 + \frac{2\beta\lambda_{\mathrm{d}}^2(t-t_{\mathrm{md0}})}{\tau_{\mathrm{p}}}}}. \tag{S15}$$

S1.2.2 Marginal/reaction-limited crossover

In the marginal regime, the reaction rate $S(t)$ and the thickness $h(t)$ are given by eqs. (S9) and (S10), respectively. Without applied mechanical stress, the system size is constant, $L(t) = L_0$. The thickness of the product-rich phase at the crossover between the marginal to reaction-limited regimes has the form

$$h_{\mathrm{mr0}} = L_0 - \lambda_{\mathrm{d}}, \tag{S16}$$

see eq. (S8). The time at the marginal/reaction-limited crossover is derived as

$$t_{\mathrm{mr0}} = \tau_{\mathrm{p}} \log\left(1 + \frac{L_0 - \lambda_{\mathrm{d}}}{\alpha \lambda_{\mathrm{d}}}\right) \tag{S17}$$

by using $h_{\mathrm{m}}(t_{\mathrm{mr0}}) = h_{\mathrm{mr0}}$ (see eq. (S11) and (S16)). The reaction rate in the reaction-limited regime is derived as

$$S_{\mathrm{r}}(t) = k \psi_{\mathrm{A2}}^{\mathrm{r}} \psi_{\mathrm{B2}}^{\mathrm{r}} \lambda_{\mathrm{d}} \mathrm{e}^{\frac{t_{\mathrm{mr0}}}{\tau_{\mathrm{p}}} + (1-\alpha)\frac{t - t_{\mathrm{mr0}}}{\tau_{\mathrm{p}}}} \tag{S18}$$

by using eq. (S5) with the continuity at the crossover, $S_{\mathrm{r}}(t_{\mathrm{mr0}}) = S_{\mathrm{m}}(t_{\mathrm{mr0}})$. Solving eq. (S1) with eq. (S18) and $v(t) = 0$ leads to the thickness $h_{\mathrm{r}}(t)$ of the product-rich phase in the form

$$h_{\mathrm{r}}(t) = h_{\mathrm{mr0}} + \frac{\alpha}{1-\alpha} \lambda_{\mathrm{d}} \mathrm{e}^{\frac{t_{\mathrm{mr0}}}{\tau_{\mathrm{p}}}} \left(\mathrm{e}^{(1-\alpha)\frac{t - t_{\mathrm{mr0}}}{\tau_{\mathrm{p}}}} - 1\right). \tag{S19}$$

S1.2.3 Reaction-limited / diffusion-limited crossover

In the reaction-limited regime, the reaction rate $S(t)$ and the thickness $h(t)$ of the product-rich phase in the reaction-limited regime are given by eqs. (S18) and (S19). The thickness of the product-rich phase at the reaction-limited/diffusion-limited crossover is derived as

$$h_{\mathrm{rd0}} = \frac{\sqrt{4\beta(1-\alpha)\lambda_{\mathrm{d}}^2 + (\alpha L_0)^2} - \alpha L_0}{2(1-\alpha)} \tag{S20}$$

by using eqs. (S4), (S18), and (S19). By using the relationship $h_{\mathrm{r}}(t_{\mathrm{rd0}}) = h_{\mathrm{rd0}}$, the time at the reaction-limited/diffusion-limited crossover is derived as

$$t_{\mathrm{rd0}} = t_{\mathrm{mr0}} + \frac{\tau_{\mathrm{p}}}{1-\alpha} \log\left(\frac{\sqrt{4\beta(1-\alpha)\lambda_{\mathrm{d}}^2 + (\alpha L_0)^2} - \alpha L_0}{2(L_0 - (1-\alpha)\lambda_{\mathrm{d}})}\right), \tag{S21}$$

see eqs. (S19) and (S20).

In the diffusion-limited regime, the thickness of the product-rich phase is derived as

$$h_{\mathrm{d}}(t) = \sqrt{h_{\mathrm{rd0}}^2 + \frac{2\beta\lambda_{\mathrm{d}}^2 (t - t_{\mathrm{rd0}})}{\tau_{\mathrm{p}}}} \tag{S22}$$

by solving eq. (S1) with $v(t) = 0$ and the continuity of the thickness, $h_{\mathrm{d}}(t_{\mathrm{rd0}}) = h_{\mathrm{rd0}}$. Substituting eq. (S22) into eq. (S4) leads to the reaction rate in the diffusion-limited regime

$$S_{\mathrm{d}}(t) = D_{\mathrm{B}} \frac{\psi_{\mathrm{B1}}^{\mathrm{d}}}{\sqrt{h_{\mathrm{rd0}}^2 + \frac{2\beta\lambda_{\mathrm{d}}^2(t - t_{\mathrm{rd0}})}{\tau_{\mathrm{p}}}}}. \tag{S23}$$

Eqs. (S22) and (S23) are equal to eqs. (S14) and (S15) except for the boundary condition.

S1.2.4 System size at cross-section

The system size L_2^* at the intersection between the three crossover thicknesses, h_{md0}, h_{mr0}, and h_{rd0}, is derived as

$$L_2^* = \alpha\lambda_{\mathrm{d}}\left(\sqrt{\frac{1}{4} + \frac{\beta}{\alpha^2}} - \frac{1}{2}\right) + \lambda_{\mathrm{d}} \tag{S24}$$

by using eqs. (S12) and (S16). The system size L_1^* at $h_{\mathrm{rd0}} = L_0$ is derived as

$$L_1^* = \sqrt{\beta}\lambda_{\mathrm{d}}. \tag{S25}$$

For cases in which the penetration of reactant A molecules into reactant B solid is prohibitive, $\alpha \to 0$, the crossover thicknesses have the simple relationship,

$$h_{\mathrm{rd0}} = h_{\mathrm{md0}} = L_1^*. \tag{S26}$$

S1.3 Reaction rate and regime diagram with applied mechanical stress

S1.3.1 Crossover time t_{c}

In the short time scales, $h(t) \approx 0$, eq. (S1) has an approximate form

$$\frac{d}{dt}h(t) = \frac{S(t)}{1 - \psi_{\mathrm{A1}} - \psi_{\mathrm{B1}}}. \tag{S27}$$

Eq. (S27) suggests that the flow does not significantly affect the dynamics of the system and the results of S1.2 is effective. In the long time scales, $\frac{dh(t)}{dt} \approx 0$, eq. (S1) has an approximate form

$$\frac{S(t)}{1-\psi_{\mathrm{A1}}-\psi_{\mathrm{B1}}}-v(t)=0, \tag{S28}$$

implying that the effects of the flow are significant only in these time scales. We define the crossover time t_{c}, where the effect of the material flow is significant for $t>t_{\mathrm{c}}$ but not for $t<t_{\mathrm{c}}$.

S1.3.2 Reaction rate and thickness of product-rich phase for $t>t_{\mathrm{c}}$

In the marginal regime, the reaction rate is given by eq. (S10) even for $t>t_{\mathrm{c}}$ because it is not affected by applied mechanical stress, see eqs. (S6) and (S9). The thickness of the product-rich phase in this regime is derived as

$$\frac{h_{\mathrm{m}}(t)}{\lambda_{\mathrm{d}}}=\left(\frac{\alpha\sigma_{\mathrm{p}}}{\sigma_{\perp}}\right)^{\frac{1}{3}}\mathrm{e}^{\frac{t}{3\tau_{\mathrm{p}}}} \tag{S29}$$

by substituting eq. (S10) into eq. (S28) with eq. (S2). The crossover time t_{c} is thus calculated by the crossover condition

$$\alpha\lambda_{\mathrm{d}}\left(\mathrm{e}^{\frac{t_{\mathrm{c}}}{\tau_{\mathrm{p}}}}-1\right)=\left(\frac{\alpha\sigma_{\mathrm{p}}}{\sigma_{\perp}}\right)^{\frac{1}{3}}\mathrm{e}^{\frac{t_{\mathrm{c}}}{3\tau_{\mathrm{p}}}}. \tag{S30}$$

In the diffusion-limited regime, the thickness of the product-rich phase is derived as

$$\frac{h_{\mathrm{d}}(t)}{\lambda_{\mathrm{d}}}=\left(\frac{\beta\sigma_{\mathrm{p}}}{\sigma_{\perp}}\right)^{\frac{1}{4}} \tag{S31}$$

by solving eq. (S28) with eq. (S2) and (S4). Substituting eq. (S31) into eq. (S4) leads to the reaction rate in the form

$$S_{\mathrm{d}}(t)=D_{\mathrm{B}}\frac{\psi_{\mathrm{B1}}^{\mathrm{d}}}{\lambda_{\mathrm{d}}}\left(\frac{\sigma_{\perp}}{\beta\sigma_{\mathrm{p}}}\right)^{\frac{1}{4}}. \tag{S31}$$

When the crossover time t_{c} is in the diffusion-limited regime, $t_{\mathrm{c}}>t_{\mathrm{md}}$, it is calculated by the crossover condition

$$D_{\mathrm{B}}\frac{\psi_{\mathrm{B1}}^{\mathrm{d}}}{\sqrt{h_{\mathrm{md}}^{2}+\frac{2\beta\lambda_{\mathrm{d}}^{2}(t_{\mathrm{c}}-t_{\mathrm{md}})}{\tau_{\mathrm{p}}}}}=\left(\frac{\beta\sigma_{\mathrm{p}}}{\sigma_{\perp}}\right)^{\frac{1}{4}}. \tag{S32}$$

S1.3.3 Crossover time t_{md}

For the case of $t_{\mathrm{c}} > t_{\mathrm{md}}$,the crossover time t_{md} is equal to t_{md0}, because the effect of applied mechanical stress is not significant. For the case of $t_{\mathrm{c}} < t_{\mathrm{md}}$, the crossover time t_{md} is derived as

$$\frac{t_{\mathrm{md}}}{\tau_{\mathrm{p}}} = \log\left(\frac{\beta^{3/4}\sigma_{\perp}^{1/4}}{\alpha\sigma_{\mathrm{p}}^{1/4}}\right), \tag{S33}$$

by the continuity of the thickness of the product-rich phase at the crossover, $h_{\mathrm{m}}(t_{\mathrm{md}}) = h_{\mathrm{d}}(t_{\mathrm{md}})$, see eqs. (S29) and (S31). The applied mechanical stress σ_{r} at the crossover is derived as

$$\frac{\sigma_{\mathrm{r}}}{\sigma_{\mathrm{p}}} = \frac{\alpha^4}{\beta^3}\left(\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{\beta}{\alpha^2}}\right)^4. \tag{S34}$$

S1.4 Acceleration of reaction by material flow driven by applied mechanical stress

S1.4.1 Reaction completion time

To study the acceleration of mechanochemical reactions by material flow, we analyze the reaction completion time t_{s} of the reaction

$$h(t_{\mathrm{s}}) = L(t_{\mathrm{s}}), \tag{S35}$$

at which the entire system becomes the product-rich phase. Because of the complexity of the problem, we limit our discussion to the case of $L_0 > L_2^*$ and $\alpha < \beta^{1/2}$.

S1.4.2 Five mechanical regime

Regime I: $\sigma_{\perp} < \sigma_0$

The flow does not affect the dynamics of the system for the entire time scale (Fig. S1). The crossover stress σ_0 is has the form

$$\frac{\sigma_0}{\sigma_{\mathrm{p}}} = \frac{\beta\lambda_{\mathrm{d}}^4}{L_0^4}, \tag{S36}$$

which is derived by the relationship $L_0 = h_{\mathrm{d}}(t_{\mathrm{c}})$ at $\sigma_{\perp} = \sigma_0$, see eq. (S31).

The reaction completion time t_{s} is derived as

$$\frac{t_\mathrm{s}-t_\mathrm{md0}}{\tau_\mathrm{p}}=\frac{1}{2}\left(\frac{L_0^2}{\beta\lambda_\mathrm{d}^2}-1\right) \tag{S37}$$

by using $L_0 = h_\mathrm{d}(t_\mathrm{s})$, see eq. (S14).

Regime II. $\sigma_0 < \sigma_\perp < \sigma_\mathrm{r}$

The reaction is diffusion-limited in the time scales, $t > t_\mathrm{c}$, at which the effect of the flow becomes significant. The crossover time t_c is derived as

$$\frac{t_\mathrm{c}-t_\mathrm{md0}}{\tau_\mathrm{p}}=\frac{1}{2}\left(\left(\frac{\sigma_\mathrm{p}}{\beta\sigma_\perp}\right)^{\frac{1}{2}}-1\right), \tag{S38}$$

by using the continuity of the thickness $h(t)$ at $t = t_\mathrm{c}$, see eq. (S32). The thickness of the system is L_0 for $t < t_\mathrm{c}$ and is derived as

$$L(t)=L_0-\lambda_\mathrm{d}\sigma_\perp^{\frac{1}{4}}\beta^{\frac{3}{4}}\frac{t-t_\mathrm{c}}{\tau_\mathrm{p}} \tag{S39}$$

for $t > t_\mathrm{c}$ by solving eq. (S3) with eq. (S31). The reaction completion time t_s is derived by using eq. (S35) as

$$\frac{t_\mathrm{s}-t_\mathrm{md0}}{\tau_\mathrm{p}}=\frac{L_0}{\beta^{\frac{3}{4}}\lambda_\mathrm{d}}\left(\frac{\sigma_\mathrm{p}}{\sigma_\perp}\right)^{\frac{1}{4}}-\frac{1}{2}\frac{1}{\beta^{\frac{1}{2}}}\left(\frac{\sigma_\mathrm{p}}{\sigma_\perp}\right)^{\frac{1}{2}}-\frac{1}{2}, \tag{S40}$$

see eqs. (S31) and (S39).

Regime III: $\sigma_\mathrm{r} < \sigma_\perp < \sigma_\mathrm{tri}$

The reaction regime is marginal at $t = t_\mathrm{c}$, at which the effect of the flow becomes significant, and then crossovers to the diffusion-limited regime. The crossover time t_c is derived as

$$\frac{t_\mathrm{c}}{\tau_\mathrm{p}}=\log\left(1+\frac{\sigma_\mathrm{p}^{1/2}}{\alpha\sigma_\perp^{1/2}}\right) \tag{S41}$$

by using the continuity of the thickness $h(t)$ at $t = t_\mathrm{c}$, eq. (30), for $\sigma_\perp/\sigma_\mathrm{p} < \alpha^{-2}$.

The thickness $L(t)$ of the system is L_0 for $t < t_\mathrm{c}$,

$$L(t)=L_0-\frac{\sigma_\perp}{\sigma_\mathrm{p}}\frac{h^3(t)-h^3(t_\mathrm{c})}{\lambda_\mathrm{d}^2} \tag{S42}$$

for $t_\mathrm{c} < t < t_\mathrm{md}$, and

$$L(t) = L(t_\mathrm{md}) - \lambda_\mathrm{d}\sigma_\perp^{\frac{1}{4}}\beta^{\frac{3}{4}}\frac{t - t_\mathrm{md}}{\tau_\mathrm{p}} \tag{S43}$$

for $t > t_\mathrm{md}$, which are derived by using eq. (S3) with eqs. (S29) and (S31).

The reaction completion time t_s is derived as

$$\frac{t_\mathrm{s} - t_\mathrm{md}}{\tau_\mathrm{p}} = \frac{L_0}{\beta^{\frac{3}{4}}}\frac{\sigma_\mathrm{p}^{\frac{1}{4}}}{\sigma_\perp^{\frac{1}{4}}} - 1, \tag{S44}$$

by using eq. (S35) with eqs. (S31) and (S43), where we omitted higher order terms with respect to $\sigma_\perp^{-1}$.

Regime IV: $\sigma_\mathrm{tri} < \sigma_\perp < \sigma_\mathrm{th}$

The reaction regime changes from the marginal to the reaction-limited and then to the diffusion-limited. The time at the marginal/reaction-limited crossover has the form

$$\frac{t_\mathrm{mr}}{\tau_\mathrm{p}} = \log\left(\frac{L_0 - \lambda_\mathrm{d}}{\alpha\lambda_\mathrm{d}}\right), \tag{S45}$$

which is derived by using the condition

$$L(t_\mathrm{mr}) - h(t_\mathrm{mr}) = \lambda_\mathrm{d} \tag{S46}$$

with an approximation $L_0 - \lambda_\mathrm{d} < \alpha\lambda_\mathrm{d}$, see eqs. (S29) and (S42).

The mechanical stress σ_tri at the cross-section of the three crossover lines is derived as

$$\frac{\sigma_\mathrm{tri}}{\sigma_\mathrm{p}} = \frac{(L_0 - \lambda_\mathrm{d})^4}{\lambda_\mathrm{d}^4\beta^3} \tag{S47}$$

by using the condition $t_\mathrm{mr} = t_\mathrm{md}$.

The thickness $h(t)$ of the product-rich phase in the reaction-limited regime is derived as

$$h(t) = \lambda_\mathrm{d}\left(\frac{L_0 - \lambda_\mathrm{d}}{\lambda_\mathrm{d}}\right)^{\frac{1}{3}}\left(\frac{\sigma_\mathrm{p}}{\sigma_\perp}\right)^{\frac{1}{3}}\mathrm{e}^{\frac{(1-\alpha)(t-t_\mathrm{mr})}{\tau_\mathrm{p}}}, \tag{S48}$$

by solving eq. (S28) and by using the continuity of $h(t)$ at $t = t_\mathrm{mr}$, see eqs. (S10) and (S29).

The time t_{rd} at the reaction-limited/diffusion-limited crossover is derived as

$$\frac{t_{\mathrm{rd}}-t_{\mathrm{mr}}}{\tau_{\mathrm{p}}}=\frac{1}{1-\alpha}\log\left(\frac{\beta^{\frac{3}{4}}\sigma_{\perp}^{\frac{1}{4}}\lambda_{\mathrm{d}}}{(L_0-\lambda_{\mathrm{d}})\sigma_{\mathrm{p}}^{\frac{1}{4}}}\right) \tag{S49}$$

by using the continuity of the thickness $h(t)$ at $t=t_{\mathrm{rd}}$, see eqs. (S31) and (S48).

The thickness $L(t)$ of the system is L_0 for $t<t_{\mathrm{c}}$, is given by eq. (S42) for $t_{\mathrm{c}}<t<t_{\mathrm{mr}}$,

$$L(t)=1+h(t_{\mathrm{mr}})-\frac{1}{1-\alpha}\frac{\sigma_{\perp}}{\sigma_{\mathrm{p}}}\frac{h^3(t)-h^3(t_{\mathrm{mr}})}{\lambda_{\mathrm{d}}^2} \tag{S50}$$

for $t_{\mathrm{mr}}<t<t_{\mathrm{rd}}$ and

$$L(t)=L(t_{\mathrm{rd}})-\lambda_{\mathrm{d}}\sigma_{\perp}^{\frac{1}{4}}\beta^{\frac{3}{4}}\frac{t-t_{\mathrm{rd}}}{\tau_{\mathrm{p}}} \tag{S51}$$

for $t>t_{\mathrm{rd}}$, which are derived by solving eq. (S3) with eqs. (S31) and (S48).

The reaction completion time t_{s} is derived as

$$\frac{t_{\mathrm{s}}-t_{\mathrm{rd}}}{\tau_{\mathrm{p}}}=\frac{1}{1-\alpha}\left(\frac{1}{\beta^{\frac{3}{4}}}\frac{L_0-\alpha\lambda_{\mathrm{d}}}{\lambda_{\mathrm{d}}}\left(\frac{\sigma_{\mathrm{p}}}{\sigma_{\perp}}\right)^{\frac{1}{4}}-1\right) \tag{S52}$$

by using eqs. (S31) and (S51).

Regime V: $\sigma_{\perp}>\sigma_{\mathrm{th}}$

The reaction regime is marginal in the time scales, $t>t_{\mathrm{c}}$, at which the effect of the flow becomes significant, and then crossover to reaction-limited without entering to the diffusion limited regime. The maximum mechanical stress σ_{in} at which the mechanochemical reaction can be diffusion-limited is written as

$$\frac{\sigma_{\mathrm{th}}}{\sigma_{\mathrm{p}}}=\frac{(L_0-\alpha\lambda_{\mathrm{d}})^4}{\beta^3\lambda_{\mathrm{d}}^4}, \tag{S53}$$

which is derived by the condition $t_{\mathrm{s}}=t_{\mathrm{rd}}$, see eq. (S52).

The reaction completion time is derived as

$$\frac{t_{\mathrm{s}}-t_{\mathrm{rd}}}{\tau_{\mathrm{p}}}=\frac{1}{1-\alpha}\log\left(\frac{L_0-\alpha\lambda_{\mathrm{d}}}{L_0-\lambda_{\mathrm{d}}}\right) \tag{S54}$$

by using eq. (S35) with eqs. (S48) and (S50).

S1.4.3 Differential reaction completion time

The difference between the maximum and minimum reaction completion times has an asymptotic form

$$\frac{\Delta t_{\mathrm{s}}}{\tau_{\mathrm{p}}} = \frac{1}{2}\left(\frac{L_0}{L_1^*}\right)^2 - \frac{1}{2} - \log\frac{L_0}{L_1^*} \tag{S55}$$

for the case of $\alpha \ll 1$. The extent of the acceleration of mechanochemical reactions by the flow thus increases with increasing thickness L_0/L_1^* of the system, although the mechanical stress σ_{th} necessary to achieve the maximum acceleration also increases, see eq. (S53).

S1.5 Reaction kinetics of remnant reactants

We have defined the reaction completion time t_s by the condition that the entire system becomes the product-rich phase, see eq. (S35). However, reactant molecules that remain unreacted are dissolved in the product-rich phase even at $t = t_{\mathrm{s}}$ although their volume fractions are rather small. For $t > t_{\mathrm{s}}$, the reactant volume fractions are not fixed because reactant-rich solids no longer exist.

In the reaction-limited regime, the time evolution equation of the reactant volume fraction is

$$\frac{d}{dt}\psi_{\mathrm{B}}(t) = -k\psi_{\mathrm{A}}(t)\psi_{\mathrm{B}}(t) \tag{S56}$$

with $\psi_{\mathrm{A}}(t) = \psi_{\mathrm{B}}(t)$ because of the symmetry of the system. We impose the initial condition $\psi_{\mathrm{B}}(t_{\mathrm{s}}) = \psi_{\mathrm{B1}}^{\mathrm{r}}$ to solve eq. (S56). By solving eq. (S56), the reactant volume fraction is derived as

$$\psi_B(t) = \frac{\psi_{\mathrm{B1}}^{\mathrm{r}}}{1 + k\psi_{\mathrm{B1}}^{\mathrm{r}}(t - t_{\mathrm{s}})}, \tag{S57}$$

which is independent of applied mechanical stress.

In the diffusion-limited regime, the time evolution equation of the reactant volume fraction has the form

$$\frac{d}{dt}\left(\frac{1}{2}\psi_{\mathrm{Bh}}(t)h(t)\right) = -D_{\mathrm{B}}\frac{\psi_{\mathrm{Bh}}(t)}{h(t)} - \frac{1}{2}\psi_{Bh}(t)v(t), \tag{S58}$$

with $\psi_{\mathrm{Bh}}(t) = \psi_{\mathrm{B}}(h(t), t)$ because the volume fraction is a linear function of the distance z, $\psi_{\mathrm{B}}(z,t) = \psi_{\mathrm{Bh}}(t)\frac{z}{h(t)}$. We impose the initial condition $\psi_{\mathrm{Bh}}(t_{\mathrm{s}}) = \psi_{\mathrm{B1}}^{\mathrm{d}}$ to solve eq. (65).

The thickness $h(t)$ of the product-rich phase is derived by solving eq. (S1) with $S(t) = 0$. By solving eq. (S58), the reactant volume fraction is derived as

$$\psi_{\mathrm{Bh}}(t) = \psi_{\mathrm{B1}}^{\mathrm{d}} e^{-\frac{2D_{\mathrm{B}}(t-t_{\mathrm{s}})}{h^2(t_{\mathrm{s}})}\frac{2D_{\mathrm{B}}\sigma_{\perp}(t-t_{\mathrm{s}})^2}{\tau_{\mathrm{p}}\lambda_{\mathrm{d}}^2\sigma_{\mathrm{p}}}}. \tag{S59}$$

Eq. (S59) demonstrates that the reaction is accelerated by the applied mechanical stress $\sigma_{\perp}$ in the diffusion-limited regime also for $t > t_{\mathrm{s}}$.

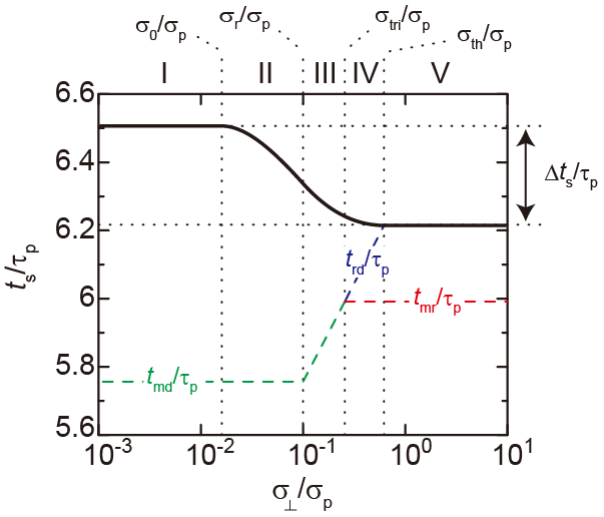


Figure S1 Reaction completion time vs applied mechanical stress. The reaction completion time t_s is shown as a function of mechanical stress for $\alpha = 0.01$ and $\beta = 10.0$. This result was obtained by using eqs. (S37), (S40), (S44), (S52), and (S54), which are effective in region I – V, respectively. The solid lines are the times at the marginal/diffusion-limited (green), marginal/reaction-limited (red), and reaction-limited/diffusion-limited (purple) crossovers. Δt_s is the maximum variation of reaction completion time due to the applied mechanical stress.

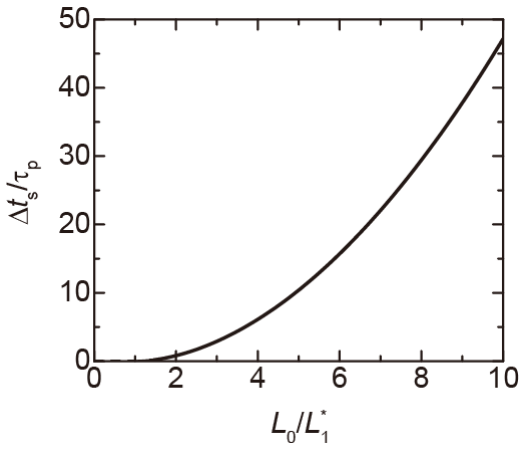


Figure S2 Reaction acceleration vs system size. The maximum variation Δt_s of reaction completion time due to applied mechanical stress is shown as a function of the system size L_0, rescaled by the threshold value L_1^*. This result is derived by eq. (S55).