Mathematical modeling of the reaction of metal oxides with methane

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Nomenclature

α	metal oxides phase
β	product phase (after reduction)
R_0	radius of the original whole metal oxides particle
r	radius of the unreduced metal oxides particle
x	thickness of the product layer
ξ	reduction extent
ξ_1	reduction extent of the first reaction
ξ_2	reduction extent of the second reaction
t	time
λ_1, λ_2	coefficients depending on the oxygen loss of each single reaction
K_{eq}	equilibrium constant
R	gas constant
T	absolute temperature with Kelvin
T_0	initial temperature with Kelvin
M	molecule weight of metal oxides
ρ	density of metal oxides
v_r	the overall reaction rate per unit area
K_r^f , K_r^b	the defined reaction rate coefficients
K_C	the reaction rate coefficient of methane cracking
K_r^0	constant independent of temperature
$J_{CH_4}^{\beta}$	flux of CH_4 in the β phase

ΔE_{app} apparent activation energy of reduction

P_{CH_4} content of CH_4

P_{CO} content of CO

P_{H_2O} content of H_2O

$P^{eq}_{CH_4}$ CH_4 content in equilibrium

$D^{\beta}_{CH_4}$ the diffusion coefficient of CH_4

m, n, z the reaction orders.

η temperature-increasing rate

Formula derivation

3.1. Interface chemical reaction

3.1.1. Spherical particles

The ξ (reduction extent) at r can be expressed by using the following equation.

$$\xi = \frac{V_R - V_r}{V_R} = 1 - \frac{V_r}{V_R} = 1 - \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi R_0^3}$$

Then, equation (2) $\xi = 1 - \left(\frac{r}{R_0}\right)^3$ was obtained. One can be obtained through the derivation of Eq. (2) to time t.

$$\frac{d\xi}{dt} = -\frac{3r^2}{R_0^{\ 3}}\frac{dr}{dt} \tag{3}$$

Eq. (1) can be calculated as follow.

$$v_r^f = K_r^f P^m{}_{CH4}(\alpha/\beta) \tag{4}$$

$$v_r^b = K_r^b P^n{}_{CO}(\alpha/\beta) P^z{}_{H2}(\alpha/\beta) \tag{5}$$

$$v_r = v_r^f - v_r^b = K_r^f P^m{}_{CH4}(\alpha/\beta) - K_r^b P^n{}_{CO}(\alpha/\beta) P^z{}_{H2}(\alpha/\beta) \tag{6}$$

When the interfacial chemical reaction is the control part of the reduction process,

$$P_{CH4}(\alpha/\beta) = P_{CH4} \tag{7}$$

$$P_{CO}(\alpha/\beta) = P_{CO} \tag{8}$$

$$P_{H2}(\alpha/\beta) = P_{H2} \tag{9}$$

The equilibrium constant of reaction (1) can be calculated as

$$K_{eq} = K_r^f / K_r^b \tag{10}$$

Substituting Eq. (10) into Eq. (6), it can be given

$$v_r = v_r^f - v_r^b = K_r^f P^m{}_{CH4(\alpha/\beta)} - \frac{K_r^f}{K_{eq}} P^n{}_{CO}(\alpha/\beta) P^z{}_{H2}(\alpha/\beta)$$

$$v_r = K_r^f (P^m{}_{CH4} - \frac{1}{K_{eq}} P^n{}_{CO} P^z{}_{H2}) \tag{11}$$

Considering the direct correlation between methane cracking and reaction rate, two cases can be drawn

1) When $\frac{k_C}{k_r^f} \geq 1$, $\frac{dr}{dt} = -\frac{M}{\rho}\frac{k_r^f}{k_C} v_r$ (12)

Eq (3) combines with Eqs. (11) and (12) to get following equation.

$$\frac{d\xi}{dt} = -\frac{3r^2}{R_0{}^3}\frac{dr}{dt} = \frac{3r^2}{R_0^3}\cdot\frac{M}{\rho}\cdot\frac{K_r^f}{K_C}V_r = \frac{3Mr^2K_r^{f2}}{R_0^3\rho K_C}\left(P_{CH_4}^m - \frac{1}{K_{eq}}P_{CO_4}^n P_{H_2}^z\right) = \frac{3M\left(1-\xi\right)^{\frac{2}{3}}K_r^{f2}}{R_0\rho K_C}\left(P_{CH_4}^m - \frac{1}{K_{eq}}P_{CO_4}^n P_{H_2}^z\right)$$

$$\frac{d\xi}{dt} = \frac{3MK_r^{f\,2}(1-\xi)^{2/3}}{R_0\rho k_C}(P^m{}_{CH4} - \frac{1}{K_{eq}} P^n{}_{CO} P^z{}_{H2}) \tag{13}$$

By integrating Eq. (13) with the initial condition of *ξ=0* when *t=0*,

$$\frac{1}{(1-\xi)^{2/3}}d\xi=\frac{3MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})d\mathrm{t}$$

$$C_1-3(1-\xi)^{1/3}=\frac{3MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}+C_2$$

When ξ=0, t=0

$$C_1-3=C_2$$

$$C_2+3-3(1-\xi)^{1/3}=\frac{3MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}+C_2$$

$$(1-\xi)^{1/3}=1-\frac{MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}$$

$$1-\xi=\left[1-\frac{MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^3$$

$$\xi=1-\left[1-\frac{MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^3,\quad \text{where } \mathrm{K_r^f}=K_{\mathrm{r}}^0\exp\left(-\frac{\Delta E_{\mathrm{app}}}{RT}\right)$$

$$\xi=1-\left(1-\frac{M\left(K_r^f\right)^2K_r^f(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})}{R_0\rho k_C}t\right)^3=1-\left(1-\frac{M\left(K_r^0\right)^2(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})}{R_0\rho k_C^0}\exp(-\frac{\Delta E_{app}}{\mathrm{R}T})t\right)^3 \tag{14}$$

where $\Delta E_{app}=2\Delta E_r-\Delta E_c$, K_r^0 and k_C^0 are temperature independent constants; ΔE_{app} is the apparent activation energy; ΔE_r and ΔE_c are the activation energy of reduction reaction and methane cracking, respectively.

2) When $\frac{k_C}{k_r^f}<1$, $\frac{dr}{dt}=-\frac{M}{\rho}\frac{k_C}{k_r^f}v_r$ (15)

$$\frac{d\xi}{dt}=-\frac{3r^2}{R_0^{\ 3}}\frac{dr}{dt}=\frac{3\mathrm{r}^2}{R_0^3}\cdot\frac{M}{\rho}\cdot\frac{K_C}{K_r^f}V_r=\frac{3M\mathrm{r}^2K_C}{R_0^3\rho}\left(P_{CH_4}^m-\frac{1}{K_{eq}}P_{CO_4}^{\mathrm{n}}P_{H_2}^{\mathrm{z}}\right)=\frac{3M\,(1-\xi)^{\frac{2}{3}}\,K_C}{R_0\rho}\left(P_{CH_4}^m-\frac{1}{K_{eq}}P_{CO_4}^{\mathrm{n}}P_{H_2}^{\mathrm{z}}\right)$$

$$\frac{1}{(1-\xi)^{2/3}}d\xi = \frac{3MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})dt$$

$$C_1 - 3(1-\xi)^{1/3} = \frac{3MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t} + C_2$$

When ξ=0，t=0

$$C_1 - 3 = C_2$$

$$C_2 + 3 - 3(1-\xi)^{1/3} = \frac{3MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t} + C_2$$

$$(1-\xi)^{1/3} = 1 - \frac{MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}$$

$$1-\xi = \left[1 - \frac{MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^3$$

$$\xi = 1 - \left[1 - \frac{MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^3, \text{ where } \mathrm{K}_{\mathrm{r}}^{\mathrm{f}} = K_{\mathrm{r}}^0 \exp\left(-\frac{\Delta E_{\mathrm{app}}}{RT}\right)$$

$$\xi = 1 - \left(1 - \frac{Mk_C^0(p^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}p^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})}{R_0\rho}\exp(-\frac{\Delta E_{\mathrm{C}}}{\mathrm{R}T})t\right)^3 \tag{16}$$

3.1.2. Cylindrical particles

$\xi = \frac{V_R - V_r}{V_R} = 1 - \frac{V_r}{V_R} = 1 - \frac{2\pi r^2 H}{2\pi R^2 H}$ Then, equation (17) $\xi = 1 - \left(\frac{r}{R_0}\right)^2$ was obtained. One can be obtained through the derivation of Eq. (17) to time *t*.

$$\frac{d\xi}{dt} = -\frac{2r}{R_0{}^2}\frac{dr}{dt} \tag{18}$$

1) When $\frac{k_C}{k_r^f} \geq 1$, $\frac{dr}{dt} = -\frac{M}{\rho}\frac{k_r^f}{k_C}v_r$ (19)

Eq. (20) can be deduced by combining Eqs. (11), (17), (18) and (19) yields

$$\frac{d\xi}{dt} = -\frac{2r}{R_0{}^2}\frac{dr}{dt} = \frac{2r}{R_0^2}\cdot\frac{M}{\rho}\cdot\frac{K_{\mathrm{r}}^{\mathrm{f}}}{K_C}V_r = \frac{2M\mathrm{r}K_{\mathrm{r}}^{f2}}{R_0^2\rho K_C}\left(P_{CH_4}^m - \frac{1}{K_{eq}}P_{CO_4}^{\mathrm{n}}P_{H_2}^{\mathrm{z}}\right) = \frac{2M(1-\xi)^{1/2}K_{\mathrm{r}}^{f2}}{R_0\rho K_C}\left(P_{CH_4}^m - \frac{1}{K_{eq}}P_{CO_4}^{\mathrm{n}}P_{H_2}^{\mathrm{z}}\right)$$

$$\frac{d\xi}{dt} = \frac{2M(K_r^f)^2(1-\xi)^{1/2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}} - \frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}}) \tag{20}$$

By substituting the equation mentioned above with the initial condition (*ξ=0*, *t=0*), Eq. (21) can be derived after arrangement

$$\frac{1}{(1-\xi)^{1/2}}d\xi=\frac{2MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})d\mathrm{t}$$

$$C_1-2(1-\xi)^{1/2}=\frac{2MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}+C_2$$

When ξ=0，t=0

$$C_1-2=C_2$$

$$C_2+2-2(1-\xi)^{1/2}=\frac{2MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}+C_2$$

$$(1-\xi)^{1/2}=1-\frac{MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}$$

$$1-\xi=\left[1-\frac{MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^2$$

$$\xi=1-\left[1-\frac{MK_r^{f\,2}}{R_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^2,\quad \text{where } \mathrm{K_r^f}=K_\mathrm{r}^0\exp\left(-\frac{\Delta E_{\mathrm{app}}}{RT}\right)$$

$$\xi=1-\left(1-\frac{M(K_r^0)^2(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})}{R_0\rho k_C^0}\exp(-\frac{\Delta E_{app}}{\mathrm{R}T})t\right)^2 \qquad (21)$$

where $\Delta E_{app}=2\Delta E_r-\Delta E_c$.

2) When $\frac{k_C}{k_r^f}<1$, $\frac{dr}{dt}=-\frac{M}{\rho}\frac{k_C}{k_r^f}v_r$ (22)

$$\frac{d\xi}{dt}=-\frac{2\mathrm{r}}{R_0{}^2}\frac{dr}{dt}=\frac{2\mathrm{r}}{R_0{}^2}\cdot\frac{M}{\rho}\cdot\frac{K_r^f}{K_C}V_r=\frac{2M\mathrm{r}K_C}{R_0^2\rho}\left(P_{CH_4}^m-\frac{1}{K_{eq}}P_{CO_4}^{\mathrm{n}}P_{H_2}^{\mathrm{z}}\right)=\frac{2M\left(1-\xi\right)^{1/2}K_C}{R_0\rho}\left(P_{CH_4}^m-\frac{1}{K_{eq}}P_{CO_4}^{\mathrm{n}}P_{H_2}^{\mathrm{z}}\right)$$

$$\frac{1}{(1-\xi)^{1/2}}d\xi=\frac{2MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})dt$$

$$C_1-2(1-\xi)^{1/2}=\frac{2MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}+C_2$$

*W*hen ξ=0， t=0

$$C_1-2=C_2$$

$$C_2+2-2(1-\xi)^{1/2}=\frac{2MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}+C_2$$

$$(1-\xi)^{1/2}=1-\frac{MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}$$

$$1-\xi=\left[1-\frac{MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^2$$

$$\xi=1-\left[1-\frac{MK_C}{R_0\rho}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})\mathrm{t}\right]^2,\quad \text{where } \mathrm{K_r^f}=K_\mathrm{r}^0\exp\left(-\frac{\Delta E_{\mathrm{app}}}{RT}\right)$$

$$\xi=1-\left(1-\frac{Mk_C^0(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}})}{R_0\rho}\exp(-\frac{\Delta E_C}{\mathrm{R}T})t\right)^2 \tag{23}$$

3.1.3. Lamellar particles

$$\xi=\frac{x}{H_0} \tag{24}$$

It can be derived from the derivative of Eq. (24) to time *t*.

$$\frac{d\xi}{dt}=\frac{1}{H_0}\frac{dx}{dt} \tag{25}$$

$$\text{1) When } \frac{k_C}{k_r^f}\geq 1,\ \frac{dx}{dt}=\frac{M}{\rho}\frac{k_r^f}{k_C}v_r \tag{26}$$

Then, combining Eqs. (11), (24), (25) and (26), gives

$$\frac{d\xi}{dt}=\frac{1}{H_0}\frac{dx}{dt}=\frac{1}{H_0}\frac{M}{\mathrm{\rho}}\frac{K_\mathrm{r}^f}{K_C}v_r=\frac{MK_\mathrm{r}^{f2}}{H_0\mathrm{\rho}K_C}\left(P_{CH4}^m-\frac{1}{K_{eq}}P_{CO}^nP_{H2}^z\right)$$

$$\frac{d\xi}{dt}=\frac{M(K_r^f)^2}{H_0\rho k_C}(P^m{}_{\mathrm{CH4}}-\frac{1}{K_{\mathrm{eq}}}P^n{}_{\mathrm{CO}}P^z{}_{\mathrm{H2}}) \tag{27}$$

By substituting the initial condition (*ξ=0*, *t=0*) and above equations, Eq. (28) can be obtained

$$d\xi = \frac{M(K_r^f)^2}{H_0\rho k_C}(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})dt$$

$$\xi = \frac{M(K_r^f)^2}{H_0\rho k_C}(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})t$$

$$\xi = \frac{M(K_r^0)^2(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})}{H_0\rho k_C^0}\exp(-\frac{\Delta E_{app}}{RT})t \quad (28)$$

2) When $\frac{k_C}{k_r^f} < 1$, $\frac{dx}{dt} = \frac{M}{\rho}\frac{k_C}{k_r^f}v_r$ (29)

$$d\xi = \frac{Mk_C}{H_0\rho}(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})dt$$

$$\xi = \frac{Mk_C}{H_0\rho}(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})t$$

$$\xi = \frac{Mk_C^0(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})}{R_0\rho}\exp(-\frac{\Delta E_C}{RT})t \quad (30)$$

In this study, the rate of increasing temperature η is assumed to be a constant value. The relationship between temperature (T) and time (t) can be calculated by

$$T = T_0 + \eta t \quad (33)$$

In which T_0 represents the starting temperatuyre.

By plugging Eq. (33) into Eqs. (31) and (32), the equations become

When $\frac{k_C}{k_r^f} \geq 1$,

$$\xi = 1 - \left(1 - \frac{M(K_r^0)^2(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})}{d_0\rho k_C^0}\exp(-\frac{\Delta E_{app}}{RT})\frac{T-T_0}{\eta}\right)^{S_c} \quad (34)$$

When $\frac{k_C}{k_r^f} < 1$,

$$\xi = 1 - \left(1 - \frac{Mk_C^0(P^m{}_{CH4} - \frac{1}{K_{eq}}P^n{}_{CO}P^z{}_{H2})}{d_0\rho}\exp(-\frac{\Delta E_C}{RT})\frac{T-T_0}{\eta}\right)^{S_c} \quad (35)$$

3.2. Diffusion in product layer

3.2.1. Spherical particles

$$\frac{dr}{dt} = -\frac{M}{\rho} J^{\beta}_{\mathrm{CH_4}} \tag{36}$$

According to the first Fick's law of diffusion,

$$J^{\beta}_{\mathrm{CH_4}} = -D^{\beta}_{\mathrm{CH_4}} (\frac{P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}}}{R_o - r}) \tag{37}$$

Eq. (38) is given by integrating Eqs. (2), (3), (36) and (37).

$$\frac{d\xi}{dt} = -\frac{3r^2}{R_0^{\ 3}}\frac{dr}{dt} = \frac{3r^2}{R_0^{\ 3}}\frac{M}{\rho} J^{\beta}_{CH4} = -\frac{3r^2}{R_0^{\ 3}}\frac{M}{\rho} D^{\beta}_{CH4}\left(\frac{P_{CH4}(\alpha/\beta) - P_{CH4}}{R_0 - \mathrm{r}}\right) = -\frac{3r^2 M D^{\beta}_{CH4}\left(1-\xi\right)^{2/3}}{R_0^{\ 3}\rho}\left(\frac{P_{CH4}(\alpha/\beta) - P_{CH4}}{R_0 - R_0\left(1-\xi\right)^{2/3}}\right)$$

$$\frac{d\xi}{dt} = -\frac{3MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})\frac{(1-\xi)^{2/3}}{1-(1-\xi)^{1/3}} \tag{38}$$

Eq. (38) is integrated and rearranged, then, Eq. (39) is obtained.

$$\frac{1-(1-\xi)^{1/3}}{(1-\xi)^{2/3}} d\xi = -\frac{3MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})dt$$

$$C_1\text{-}3(1-\xi)^{1/3} + \frac{3}{2}(1-\xi)^{2/3} = C_2 - \frac{3MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})\mathrm{t}$$

$$C_2 = C_1 - 3/2$$

$$-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})\mathrm{t} = \left[(1-\xi)^{1/3} - 1\right]^2$$

$$0 \le \xi \le 1 \therefore \left[(1-\xi)^{1/3} - 1\right] \le 0$$

$$\therefore (1-\xi)^{1/3} - 1 = -\sqrt{-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})\mathrm{t}}$$

$$(1-\xi)^{1/3} = 1 - \sqrt{-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})\mathrm{t}}$$

$$\xi = 1 - \left[1 - \sqrt{-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})\mathrm{t}}\right]^3$$

$$\xi = 1 - \left(1 - \sqrt{\frac{-2MD^{\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}}(\alpha/\beta) - P_{\mathrm{CH_4}})t}\right)^3 = 1 - \left(1 - \sqrt{\frac{2MD^{0\beta}_{\mathrm{CH_4}}}{R_0^{\ 2}\rho}(P_{\mathrm{CH_4}} - P^{\mathrm{eq}}_{\mathrm{CH_4}})\exp(-\frac{\Delta E_{app}}{\mathrm{R}T})t}\right)^3 \tag{39}$$

3.2.2. Cylindrical particles

Similarly, the growth rate of α in radius direction should obey Eq. (36). Combining Eqs. (17), (18), (36) and (37), Eq. (40) can be obtained.

$$\frac{d\xi}{dt}=-\frac{2\mathrm{r}}{R_0{}^2}\frac{dr}{dt}=\frac{2\mathrm{r}}{R_0{}^2}\frac{M}{\rho}J^{\beta}_{CH4}=-\frac{2\mathrm{r}}{R_0{}^2}\frac{M}{\rho}D^{\beta}_{CH4}\left(\frac{P_{CH4}(\alpha/\beta)-P_{CH4}}{R_0-\mathrm{r}}\right)=-\frac{2\mathrm{r}MD^{\beta}_{CH4}R_0\left(1-\xi\right)^{1/2}}{R_0{}^2\rho}\left(\frac{P_{CH4}(\alpha/\beta)-P_{CH4}}{R_0-R_0\left(1-\xi\right)^{1/2}}\right)$$

$$\frac{d\xi}{dt}=\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})\frac{(1-\xi)^{1/2}}{1-(1-\xi)^{1/2}} \tag{40}$$

Eq. (40) can be integrated and rearranged as

$$\frac{1-(1-\xi)^{1/2}}{(1-\xi)^{1/2}}d\xi=-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})dt$$

$$\mathrm{C}_1\text{-}2(1-\xi)^{1/2}-\xi=C_2-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})\mathrm{t}$$

$$C_2=C_1-2$$

$$-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})\mathrm{t}=\left[1-(1-\xi)^{1/2}\right]^2$$

$$0\le\xi\le1\therefore1-(1-\xi)^{1/2}\ge0$$

$$\therefore1-(1-\xi)^{1/2}=\sqrt{-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})\mathrm{t}}$$

$$(1-\xi)^{1/2}=1-\sqrt{-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})\mathrm{t}}$$

$$\xi=1-\left[1-\sqrt{-\frac{2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})\mathrm{t}}\right]^2$$

$$\xi=1-\left(1-\sqrt{\frac{-2MD^{\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})t}\right)^2=1-\left(1-\sqrt{\frac{2MD^{0\beta}_{\mathrm{CH_4}}}{R_0{}^2\rho}(P_{\mathrm{CH_4}}\text{-}P^{\mathrm{eq}}_{\mathrm{CH_4}})\exp(-\frac{\Delta Eapp}{\mathrm{R}T})t}\right)^2 \tag{41}$$

3.2.3. Lamellar particles

$$\frac{dx}{dt}=\frac{M}{\rho}J^{\beta}_{\mathrm{CH_4}} \tag{42}$$

According to the first Fick's law of diffusion, eq. (43) can be given

$$J^{\beta}_{\mathrm{CH_4}}=-D^{\beta}_{\mathrm{CH_4}}(\frac{P_{\mathrm{CH_4}}(\alpha/\beta)\text{-}P_{\mathrm{CH_4}}}{x}) \tag{43}$$

By combining Eqs. (24), (25), (42) and (43), Eq. (44) can be obtained.

$$\frac{d\xi}{dt}=\frac{1}{H_0}\frac{M}{\rho}J^{\beta}_{CH4}=-\frac{MD^{\beta}_{\mathrm{CH_4}}}{H_0{}^2\rho}\frac{P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}}}{x}=-\frac{MD^{\beta}_{\mathrm{CH_4}}}{H_0{}^2\rho}\frac{P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}}}{\xi H_0}=\text{-}\frac{MD^{\beta}_{\mathrm{CH_4}}}{H_0{}^2\rho\xi}(P_{\mathrm{CH_4}}(\alpha/\beta)-P_{\mathrm{CH_4}})$$

$$\frac{d\xi}{dt} = -\frac{MD_{CH_4}^{\beta}}{H_0{}^2\rho\xi}(P_{CH_4}(\alpha/\beta) - P_{CH_4}) \tag{44}$$

$$\xi d\xi = -\frac{MD_{CH_4}^{\beta}}{H_0{}^2\rho}(P_{CH_4}(\alpha/\beta) - P_{CH_4})dt$$

$$\frac{1}{2}\xi^2 + C_1 = -\frac{MD_{CH_4}^{\beta}}{H_0{}^2\rho}(P_{CH_4}(\alpha/\beta) - P_{CH_4})t + C_2$$

When t=0, ξ=0, C_1=C_2 can be obtained.

$$\frac{1}{2}\xi^2 = -\frac{MD_{CH_4}^{\beta}}{H_0{}^2\rho}(P_{CH_4}(\alpha/\beta) - P_{CH_4})t$$

$$\xi^2 = -\frac{2MD_{CH_4}^{\beta}}{H_0{}^2\rho}(P_{CH_4}(\alpha/\beta) - P_{CH_4})t$$

$$\xi = \sqrt{-\frac{2MD_{CH_4}^{\beta}}{H_0{}^2\rho}(P_{CH_4}(\alpha/\beta) - P_{CH_4})t}$$

$$\xi = \sqrt{\frac{-2MD_{CH_4}^{\beta}}{H_0{}^2\rho}(P_{CH_4}(\alpha/\beta) - P_{CH_4})t} = \sqrt{\frac{2MD_{CH_4}^{0\beta}}{H_0{}^2\rho}(P_{CH_4} - P_{CH_4}^{eq})\exp(-\frac{\Delta E_{app}}{RT})t} \tag{45}$$

If the shape coefficient S_c and the equivalent diameter d_0 are introduced into the model, the kinetic equation can be rewritten as

$$\xi = 1 - \left(1 - \sqrt{\frac{2MD_{CH_4}^{0\beta}}{d_0{}^2\rho}(P_{CH_4} - P_{CH_4}^{eq})\exp(-\frac{\Delta E_{app}}{RT})t}\right)^{S_c} \tag{46}$$

For non-isothermal reduction,

$$\xi = 1 - \left(1 - \sqrt{\frac{2MD_{CH_4}^{0\beta}}{d_0{}^2\rho}(P_{CH_4} - P_{CH_4}^{eq})\exp(-\frac{\Delta E_{app}}{RT})\frac{T - T_0}{\eta}}\right)^{S_c} \tag{47}$$

Table S1. List of the reported kinetic models and the corresponding calculated formula.

$^{*}\, k = A\exp\left(-\frac{\Delta E_{app}}{RT}\right)$

	Model	Integral form $g(\xi)=kt$	Explicit form	Calculated formula shown in Fig. 6
Geometrical contraction models	Contracting area (R2)	$1-(1-\xi)^{1/2}$	$\xi=1-(1-kt)^2$	$\xi=1-\left[1-2.00\times10^{-3}\exp\left(-\frac{43.634\text{J/mol}}{RT}\right)t\right]^2$, r>0.984
	Contracting volume (R3)	$1-(1-\xi)^{1/2}$	$\xi=1-(1-kt)^3$	$\xi=1-\left[1-3.43\times10^{-3}\exp\left(-\frac{10.32\text{kJ/mol}}{RT}\right)t\right]^3$, r>0.989
Diffusion models	Jander equation (2D, n=1/2)	$[1-(1-\xi)^{1/2}]^{1/2}$	$\xi=1-[1-(kt)^2]^2$	$\xi=1-\left\{1-\left[-3.33\times10^{-3}\exp\left(\frac{0.64\text{kJ/mol}}{RT}\right)t\right]^2\right\}^2$, r>0.935
	Jander equation (2D, n=2)	$[1-(1-\xi)^{1/2}]^2$	$\xi=1-[1-(kt)^{1/2}]^2$	$\xi=1-\left\{1-\left[7.18\times10^{-4}\exp\left(-\frac{0.67\text{J/mol}}{RT}\right)t\right]^{0.5}\right\}^2$, r>0.990
	Jander equation (3D, n=1/2)	$[1-(1-\xi)^{1/3}]^{1/2}$	$\xi=1-[1-(kt)^2]^3$	$\xi=1-\left\{1-\left[-4.58\exp\left(-\frac{89.75\text{kJ/mol}}{RT}\right)t\right]^2\right\}^3$, r>0.955
	Jander equation (3D, n=2)	$[1-(1-\xi)^{1/3}]^2$	$\xi=1-[1-(kt)^{1/2}]^3$	$\xi=1-\left\{1-\left[4.94\times10^{-21}\exp\left(\frac{475.61\text{kJ/mol}}{RT}\right)t\right]^{0.5}\right\}^3$, r>0.987
Nucleation and growth model	Power law (P2)	$\xi^{1/2}$	$\xi=(kt)^2$	$\xi=\left[2.82\times10^{-3}\exp\left(\frac{0.57\text{kJ/mol}}{RT}\right)t\right]^2$, r>0.841
	Power law (P3)	$\xi^{1/3}$	$\xi=(kt)^3$	$\xi=\left[2.94\times10^{-3}\exp\left(-\frac{18.49\text{J/mol}}{RT}\right)t\right]^3$, r>0.752
	Avrami-Erofe'ev (A1.5)	$[-\ln(1-\xi)]^{2/3}$	$\xi=1-\exp[-(kt)^{2/3}]$	$\xi=1-\exp\left\{\left[-5.55\times10^{-3}\exp\left(\frac{6.33\text{J/mol}}{RT}\right)t\right]^{\frac{3}{2}}\right\}$, r>0.981
	Avrami-Erofe'ev (A2)	$[-\ln(1-\xi)]^{1/2}$	$\xi=1-\exp[-(kt)^2]$	$\xi=1-\exp\left\{\left[-5.78\times10^{-3}\exp\left(-\frac{0.60\text{J/mol}}{RT}\right)t\right]^2\right\}$, r>0.966
	Avrami-Erofe'ev (A3)	$[-\ln(1-\xi)]^{1/3}$	$\xi=1-\exp[-(kt)^3]$	$\xi=1-\exp\left\{\left[-6.68\times10^{-3}\exp\left(\frac{7.40\times10^{-4}\text{J/mol}}{RT}\right)t\right]^3\right\}$, r>0.955
	Avrami-Erofe'ev (A4)	$[-\ln(1-\xi)]^{1/4}$	$\xi=1-\exp[-(kt)^4]$	$\xi=1-\exp\left\{\left[-7.47\times10^{-3}\exp\left(-\frac{7.53\text{J/mol}}{RT}\right)t\right]^4\right\}$, r>0.948

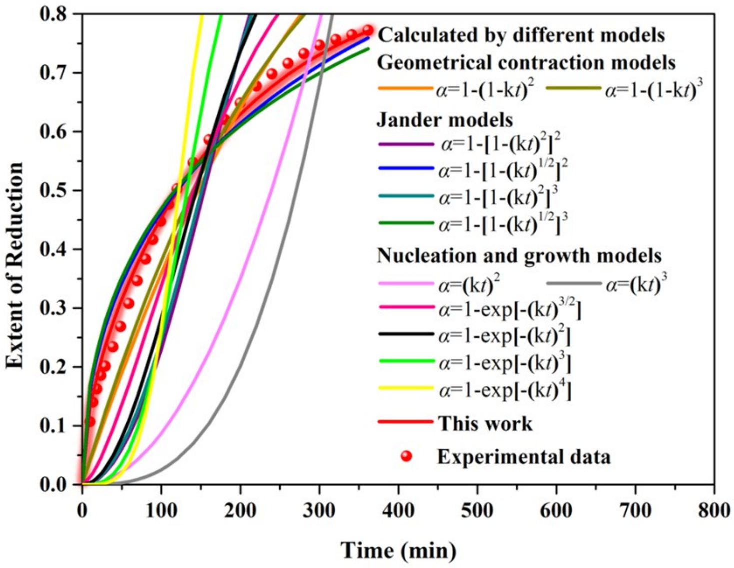

Fig. S1. Comparisons of different models' calculated results for the reduction of titania by 5vol pct CH_4-75vol pct H_2 gas mixture at 1473 K.

The derivation process of internal diffusion of gaseous product

Due to the violent cracking of methane, CH_4 is often mixed with a large percentage of hydrogen in practical applications to inhibit cracking of methane, according to the earlier reports[1-7]. Thus, the content of hydrogen presents at high levels in the reaction system. Although the gas products contain carbon monoxide and hydrogen, the change of CO content in the product layer can be negligible compared with that of H_2 content. According to the total reaction, $x\mathrm{CH_4}\left(\alpha/\beta\right)+\mathrm{MO}_x\left(\alpha\right)=\mathrm{M}\left(\beta\right)+x\mathrm{CO}\left(\alpha/\beta\right)+2x\mathrm{H_2}\left(\alpha/\beta\right)$, the content of H_2 in equilibrium is also higher than that of CO in the reaction interface. Herein, the derivation process of internal diffusion of gaseous product focuses on the internal diffusion of H_2.

1. Spherical particles

$$\frac{d_r}{d_t}=-\frac{M}{\rho}J_{gaseous\ product}^{\beta}$$

$$J_{gaseous\,product}^{\beta} = -D_{gaseous\,product}^{\beta}\left(\frac{P_{gaseous\,product} - P_{gaseous\,product}\left(\frac{\alpha}{\beta}\right)}{R_0 - r}\right) = -D_{H_2}^{\beta}$$

$$\frac{d\xi}{dt} = -\frac{3r^2 dr}{{R_0}^3 dt} = \frac{3r^2 M}{{R_0}^3 \rho} J_{gaseous\,product}^{\beta} = -\frac{3r^2 M}{{R_0}^3 \rho} D_{H_2}^{\beta}\left(\frac{P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)}{R_0 - r}\right) = -$$

$$\left[\frac{P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)}{R_0 - R_0(1-\xi)^{2/3}}\right]$$

$$\frac{d\xi}{dt} = -\frac{3MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)\frac{(1-\xi)^{2/3}}{1-(1-\xi)^{1/3}}$$

After integrating and rearranging, then,

$$\frac{1-(1-\xi)^{1/3}}{(1-\xi)^{2/3}} d\xi = -\frac{3MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) dt$$

$$C_1 - 3(1-\xi)^{1/3} + \frac{3}{2}(1-\xi)^{2/3} = C_2 - \frac{3MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t$$

$C_1 - 3/2 = C_2$

$$-\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t = \left[(1-\xi)^{1/3} - 1\right]^2$$

$$0 \le \xi \le 1, (1-\xi)^{1/3} - 1 \le 0$$

$$(1-\xi)^{1/3} = 1 - \sqrt{-\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t}$$

$$\xi = 1 - \left(1 - \sqrt{-\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t}\right)^3$$

2. Cylindrical particles

$$\frac{d_r}{d_t} = -\frac{M}{\rho} J_{gaseous\ product}^{\beta}$$

$$J_{gaseous\ product}^{\beta}$$

$$= -D_{gaseous\ product}^{\beta}\left(\frac{P_{gaseous\ product} - P_{gaseous\ product}\left(\frac{\alpha}{\beta}\right)}{R_0 - r}\right) = -D_{H_2}^{\beta}$$

$$\frac{d\xi}{dt}$$

$$= -\frac{2r\ dr}{{R_0}^2 dt} = \frac{2r\ M}{{R_0}^2 \rho} J_{gaseous\ product}^{\beta} = -\frac{2r\ M}{{R_0}^2 \rho} D_{H_2}^{\beta}\left(\frac{P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)}{R_0 - r}\right) = -$$

$$\left[\frac{P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)}{R_0 - R_0(1-\xi)^{1/2}}\right]$$

$$\frac{d\xi}{dt} = -\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)\frac{(1-\xi)^{1/2}}{1-(1-\xi)^{1/2}}$$

After integrating and rearranging, then,

$$\frac{1-(1-\xi)^{1/2}}{(1-\xi)^{1/2}} d\xi = -\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) dt$$

$$C_1 - 2(1-\xi)^{\frac{1}{2}} - \xi = C_2 - \frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t$$

$C_1 - 2 = C_2$

$$-\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t = [1-(1-\xi)^{1/2}]^2$$

$$0 \le \xi \le 1, 1 - (1-\xi)^{1/2} \ge 0$$

$$(1-\xi)^{1/2} = 1 - \sqrt{-\frac{2MD_{H_2}^{\beta}}{{R_0}^2 \rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right) t}$$

$$\xi = 1 - \left(1 - \sqrt{-\frac{2MD_{H_2}^{\beta}}{{R_0}^2\rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)t}\right)^2$$

3. Lamellar particles

$$\frac{dx}{dt} = \frac{M}{\rho}J_{gaseous\,product}^{\beta}$$

$$J_{gaseous\,product}^{\beta} = -D_{gaseous\,product}^{\beta}\left(\frac{P_{gaseous\,product} - P_{gaseous\,product}\left(\frac{\alpha}{\beta}\right)}{x}\right) = -D_{H_2}^{\beta}$$

$$\frac{d\xi}{dt} = \frac{1}{H_0}\frac{dr}{dt} = \frac{1}{H_0}\frac{M}{\rho}J_{gaseous\,product}^{\beta} = -\frac{M}{{H_0}^2\rho}D_{H_2}^{\beta}\left(\frac{P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)}{x}\right) = -\frac{M}{H}$$

$$\xi d\xi = -\frac{MD_{H_2}^{\beta}}{{H_0}^2\rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)dt$$

$$\frac{1}{2}\xi^2 + C_1 = -\frac{MD_{H_2}^{\beta}}{{H_0}^2\rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)t + C_2$$

When t=0, ξ=0, C_1=C_2 can be obtained.

$$\frac{1}{2}\xi^2 = -\frac{MD_{H_2}^{\beta}}{{H_0}^2\rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)t$$

$$\xi = \sqrt{-\frac{2MD_{H_2}^{\beta}}{{H_0}^2\rho}\left(P_{H_2} - P_{H_2}\left(\frac{\alpha}{\beta}\right)\right)t}$$

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