ESI for

Ni-based catalyst with enhanced Ni-support interaction for highly efficient CO methanation

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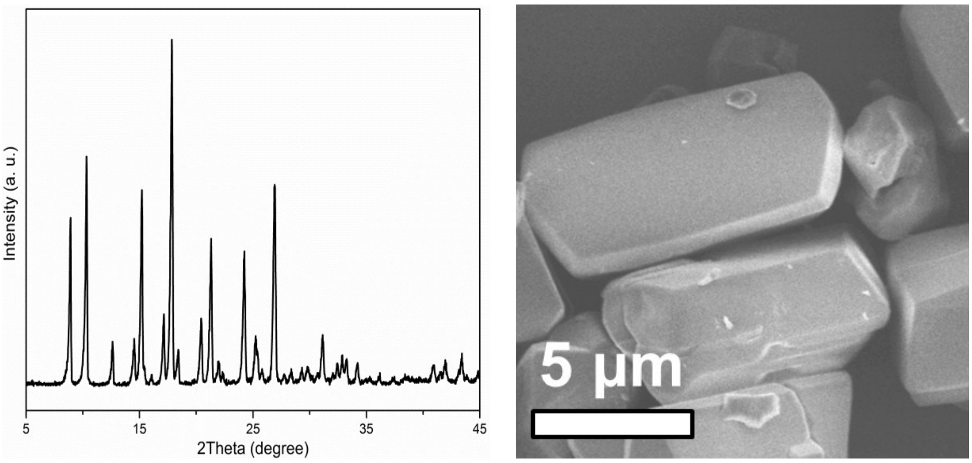


(a) (b)

Fig. S1 (a) XRD pattern and (b) SEM image of MIL-53 (Al).

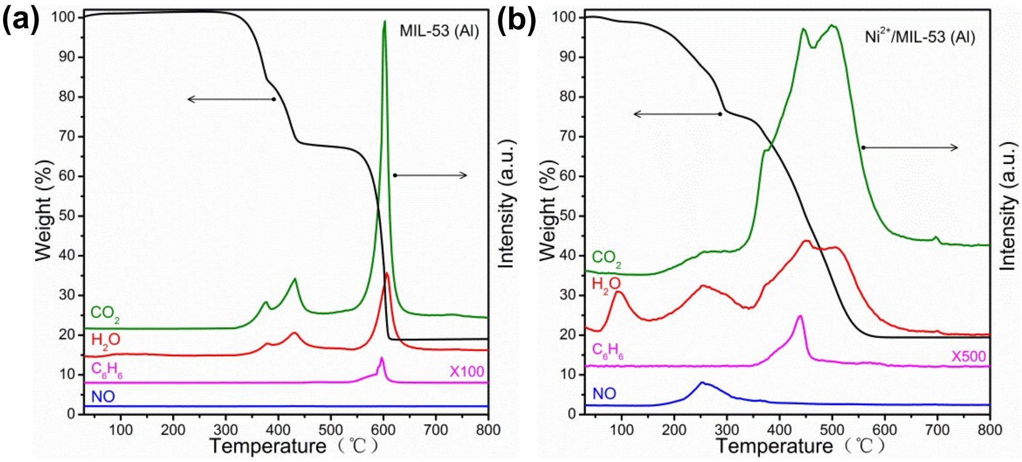


Fig. S2 TGA and corresponding mass spectrometer curves in air for (a) MIL-53 (Al) and (b) Ni^{2+}-impregnated MIL-53 (Al).

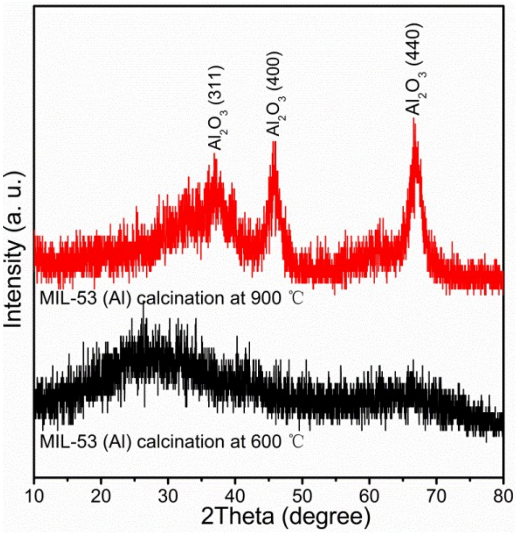
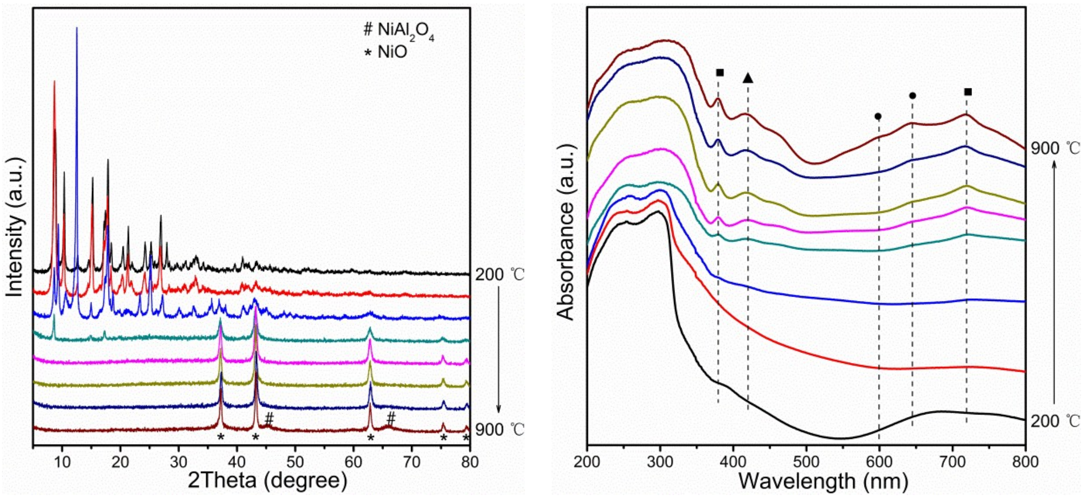


Fig. S3 XRD patterns of the samples resulted from thecalcination of MIL-53 (Al) at 600 and 900 °C.



(a) **(b)**

Fig. S4 (a) XRD patterns and (b) UV–vis–DRS spectra of the samples formed during the calcinations of the Ni^{2+}-impregnated MIL-53 (Al) from 200 to 900 °C with an interval of 100 °C (■: octahedrally coordinated Ni^{2+} in NiO lattice, ▲: octahedrally coordinated Ni^{2+} in $NiAl_2O_4$ lattice, ●: tetrahedrally coordinated Ni^{2+} in $NiAl_2O_4$ lattice).

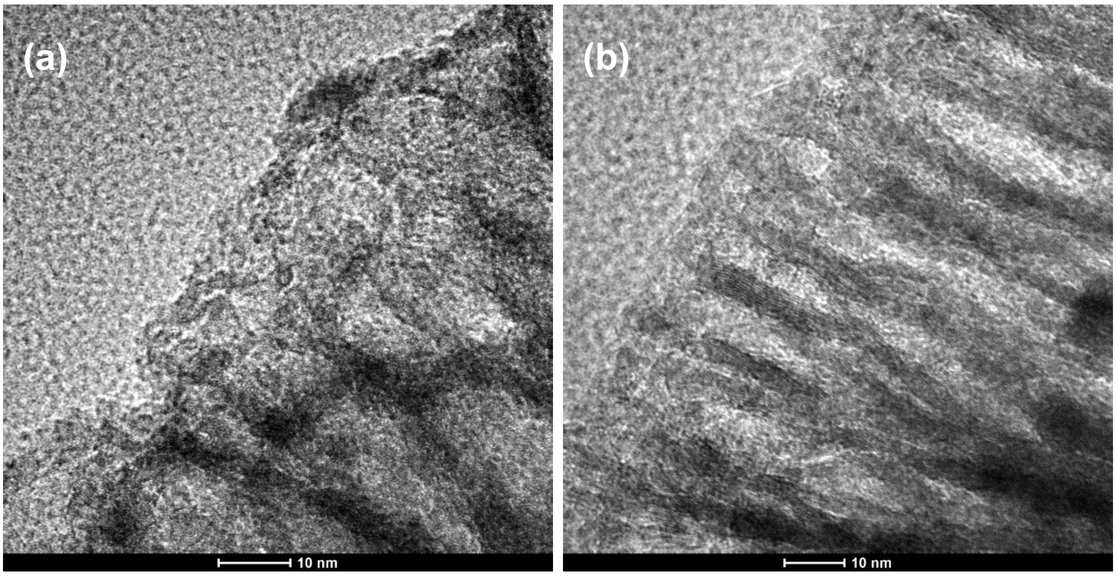


Fig. S5 High magnification TEM images of (a) NiO/Al_2O_3-M and (b) NiO/$NiAl_2O_4$-M.

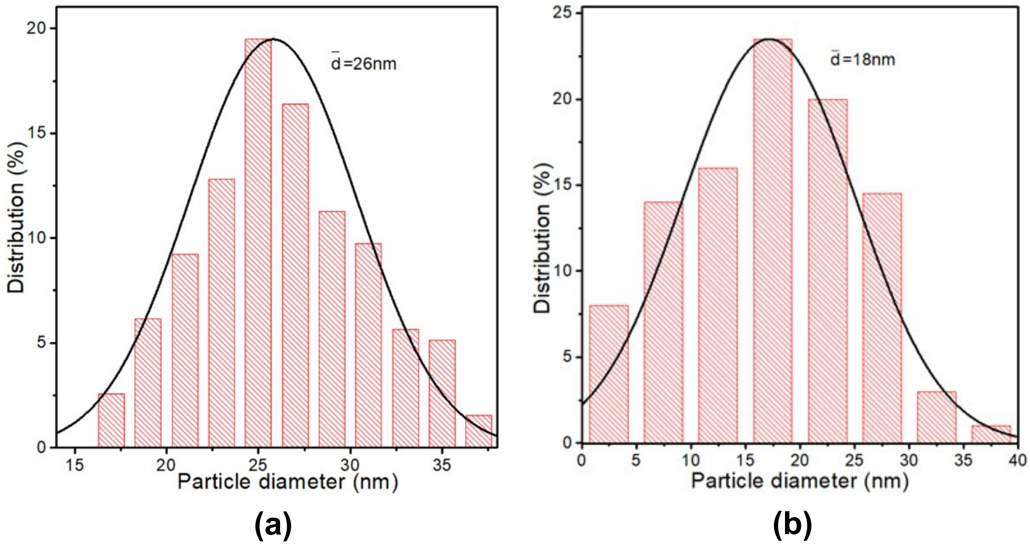


Fig. S6 Particle size distribution of (a) Ni/Al_2O_3-M and (b) $Ni/NiAl_2O_4$-M.

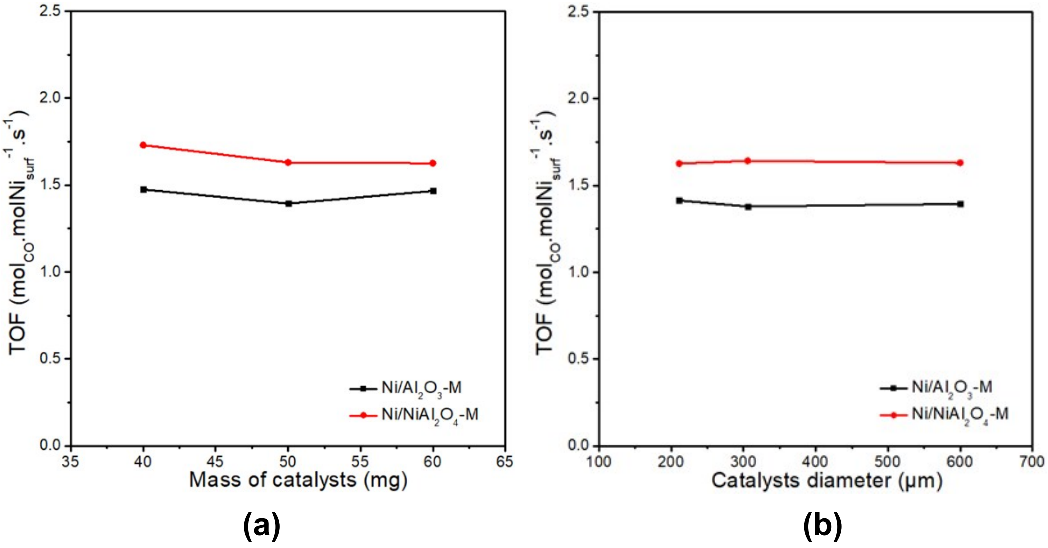


Fig. S7 Effect of (a) external and (b) internal diffusions on the catalysts.The reaction was conducted at 400 °C and 240 $Lg_{cat}^{-1}h^{-1}$.

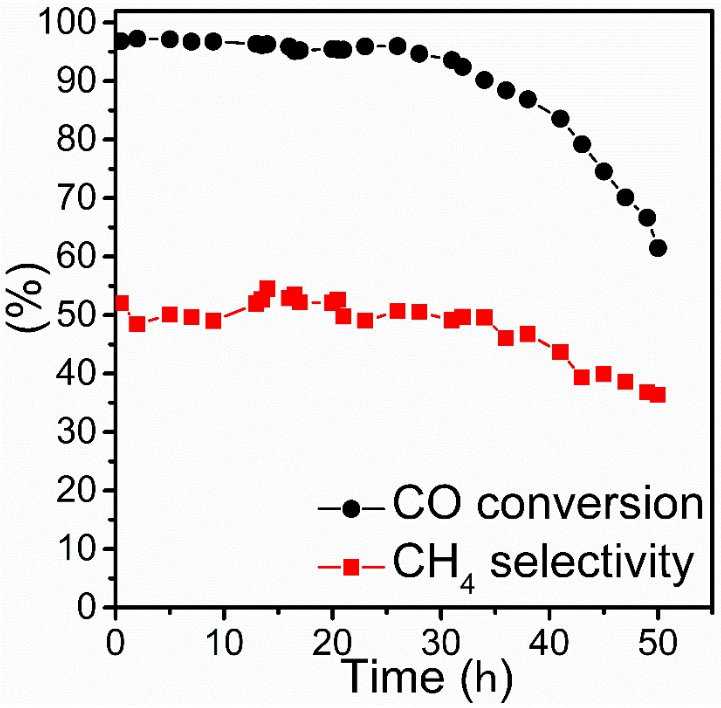


Fig. S8 Stability of Ni/Al_2O_3-C at 0.1 MPa, 400 °C and 15000 mL g^{-1} h^{-1}.

1. Mass and Heat Transfer Calculations for the methanation on Ni/Al_2O_3-M.

For PBR reaction mode (67H_2/33CO).

1.1 Mears Criterion for External Diffusion (Fogler, p841; Mears, 1971).

If $\frac{-r_A'\rho_b Rn}{k_c C_{Ab}} < 0.15$, then external mass transfer effects can be neglected.

Where $-r_A'$= reaction rate, kmol·kg_{cat}^{-1}·s^{-1};

n = reaction order;

R = catalyst particle radius, m;

ρ_b = bulk density of catalyst bed, kg·m^{-3};

=(1-ϕ) (ϕ= porosity or void fraction of packed bed);

ρ_c = solid catalyst density, kg·m^{-3};

C_{Ab} = bulk gas concentration of A, kmol·m^{-3};

k_c = mass transfer coefficient, m· s^{-1}.

$\frac{-r_A'\rho_b Rn}{k_c C_{Ab}}$ = [1.45*10^{-4}kmol·kg_{cat}^{-1}·s^{-1}]*[367.5kg·m^{-3}]*[3.0*10^{-4}m]*[1]/([0.64m·s^{-1}]*[0.0147 kmol ·m^{-3}]) = 1.7*10^{-3} < 0.15 {Mears for External Diffusion}

1.2 Weisz-Prater Criterion for Internal Diffusion (Fogler, p839).

If $C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{As}} < 1$, then internal mass transfer effects can be neglected.

Where -r'$_{A(obs)}$ = observed reaction rate, kmol·kg_{cat}^{-1}·s^{-1};

R = catalyst particle radius, m;

ρ_c = solid catalyst density, kg·m^{-3};

D_e = effective gas-phase diffusivity, m^2·s^{-1} [Fogler, p815]

$$= \frac{D_{AB}\phi_p\sigma_c}{\tau}$$

where D_{AB} = gas-phase diffusivity m^2·s^{-1}; ϕ_p = pellet porosity;

σ_c=constriction factor; τ=tortuosity.

C_{As} = gas concentration of A at the catalyst surface, kmol·m^{-3}.

$C_{WP} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{As}}$=[1.45*10^{-4}kmol·kg$_{cat}^{-1}$·s^{-1}]*[500kg·m^{-3}]*[3.0*10^{-4}m]^2/([2.65*10^{-4}m^2·s^{-1}]*[0.0147kmol·m^{-3}]) = 1.7*10^{-3}＜1

{Weisz-Prater Criterion for Internal Diffusion}

1.3 Mears Criterion for External (Interphase) Heat Transfer (Fogler, p842).

The bulk fluid temperature, T, will be virtually the same as the temperature at the external surface of the pellet when $\left|\frac{-\Delta H_r(-r_A')\rho_b RE}{h_t T_b^2 R_g}\right| < 0.15$.

Where ΔH_r = heat of reaction, kJ·mol^{-1};

E = activation energy, kJ·mol^{-1};

h_t= heat transfer coefficient between gas and pallet, kJ·m^{-2}·s^{-1}·K^{-1};

R_g=gas constant, kJ·mol^{-1}·K^{-1}.

$\left|\frac{-\Delta H_r(-r_A')\rho_b RE}{h_t T_b^2 R_g}\right|$=[242.073kJ·mol^{-1}]*[1.45*10^{-4}kmol·kg$_{cat}^{-1}$·s^{-1}]*[367.5kg·m^{-3}]*[3.0*10^{-4}m]*[80kJ·mol^{-1}]/([5.3kJ·m^{-2}·K^{-1}·s^{-1}]*[673K]^2*[8.314*10^{-3}kJ·mol^{-1}·K^{-1}]) = 1.6*10^{-5}<0.15{Mears Criterion for External (Interphase) Heat Transfer}

1.4 Mears Criterion for Combined Interphase and Intraparticle Heat and Mass Transport (Mears, 1971).

If $\frac{-r'_A R^2}{C_{Ab} D_e} < \frac{1+0.33\gamma\chi}{|n-\gamma_b\beta_b|(1+0.33n\omega)}$, which indicates that there are no interphase orintraparticle heat transfer or mass transport limitations for thepresent case.

$\gamma = \frac{E}{R_g T_s}$; $\gamma_b = \frac{E}{R_g T_b}$; $\beta_b = \frac{(-\Delta H_r)D_e C_{Ab}}{\lambda T_b}$; $\chi = \frac{(-\Delta H_r) - r'_A R}{h_t T_b}$; $\omega = \frac{-r'_A R}{k_c C_{Ab}}$

γ = Arrhenius number; β_b= heat generation function;

λ = catalyst thermal conductivity, W·m^{-1}·K^{-1};

χ = Damköhler number for interphase heat transport;

ω = Damköhler number for interphase mass transport.

$\frac{-r'_A R^2}{C_{Ab} D_e}$ =[1.45*10^{-4}kmol·kg$_{cat}^{-1}$·s^{-1}]*[3.0*10^{-4}m]^2/([0.0147kmol·m^{-3}]*[6.31*10^{-7}m^2·s^{-1}]) =1.41*10^{-3} < 3

{Mears Criterion for Interphase and Intraparticle Heat and Mass Transport }

2. Mass and Heat Transfer Calculations for the methanation on Ni/$NiAl_2O_4$-M.

For PBR reaction mode (67H_2/33CO).

2.1 Mears Criterion for External Diffusion (Fogler, p841; Mears, 1971).

If $\frac{-r_A' \rho_b R n}{k_c C_{Ab}} < 0.15$, then external mass transfer effects can be neglected.

Where $-r_A'$= reaction rate, kmol·kg$_{cat}^{-1}$·s^{-1};

n = reaction order;

R = catalyst particle radius, m;

ρ_b = bulk density of catalyst bed, kg·m^{-3};

=(1-ϕ) (ϕ= porosity or void fraction of packed bed);

ρ_c = solid catalyst density, kg·m^{-3};

C_{Ab} = bulk gas concentration of A, kmol·m^{-3};

k_c = mass transfer coefficient, m· s^{-1}.

$\frac{-r_A' \rho_b R n}{k_c C_{Ab}}$ = [2.38*10^{-4}kmol·kg$_{cat}^{-1}$·s^{-1}]*[312.5kg·m^{-3}]*[3.0*10^{-4}m]*[1]/([0.64m·s^{-1}]*[0.0147kmol·m^{-3}])= 2.4*10^{-3}< 0.15 {Mears for External Diffusion}

2.2 Weisz-Prater Criterion for Internal Diffusion (Fogler, p839).

If $C_{WP} = \frac{-r'_{A(obs)}\,\rho_c R^2}{D_e C_{As}} < 1$, then internal mass transfer effects can be neglected.

Where $-r'_{A(obs)}$ = observed reaction rate, kmol·kg_{cat}^{-1}·s^{-1};

R = catalyst particle radius, m;

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{Weisz-Prater Criterion for Internal Diffusion}

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$\gamma = \frac{E}{R_g T_s}$; $\gamma_b = \frac{E}{R_g T_b}$; $\beta_b = \frac{(-\Delta H_r) D_e C_{Ab}}{\lambda T_b}$; $\chi = \frac{(-\Delta H_r) - r'_A R}{h_t T_b}$; $\omega = \frac{-r'_A R}{k_c C_{Ab}}$

γ = Arrhenius number; β_b= heat generation function;

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$\frac{-r'_A R^2}{C_{Ab} D_e}$ = [2.38*10^{-4}kmol·kg_{cat}^{-1}·s^{-1}]*[3.0*10^{-4}m]^2/([0.0147kmol·m^{-3}]*[1.43*$10^{-6}$$m^2$·$s^{-1}$]) =1.02*1

0^{-3}＜3

{Mears Criterion for Interphase and Intraparticle Heat and Mass Transport}