Electronic Supplementary Information

An automated flow platform for accurate determination of gas-liquid-solid reaction kinetics

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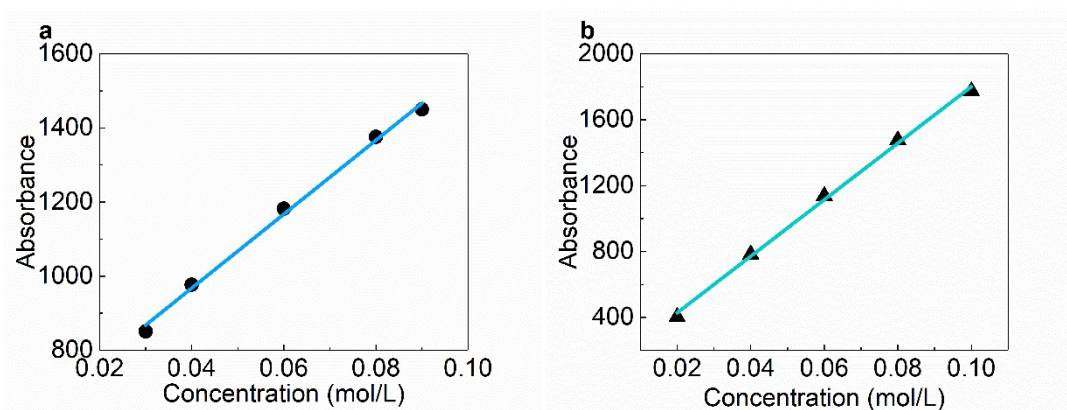
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1. Standard curve of α-methylstyrene and nitrobenzene

Fig S1. Standard curve of (a) α-methylstyrene and (b) nitrobenzene. Reaction conditions: Temperature: 26 ℃, gas pressure: 0.1 MPa; (b) Temperature: 31 ℃, gas pressure: 0.1 MPa.

Table S1. Standard curve fitting results of α-methylstyrene and nitrobenzene.

Substate	Curve fitting equation	R-square
α-methylstyrene	y=9980.8x+568.35	0.9963
nitrobenzene	y=17164x+84.28	0.998

2. UV-vis spectra of reactants and products
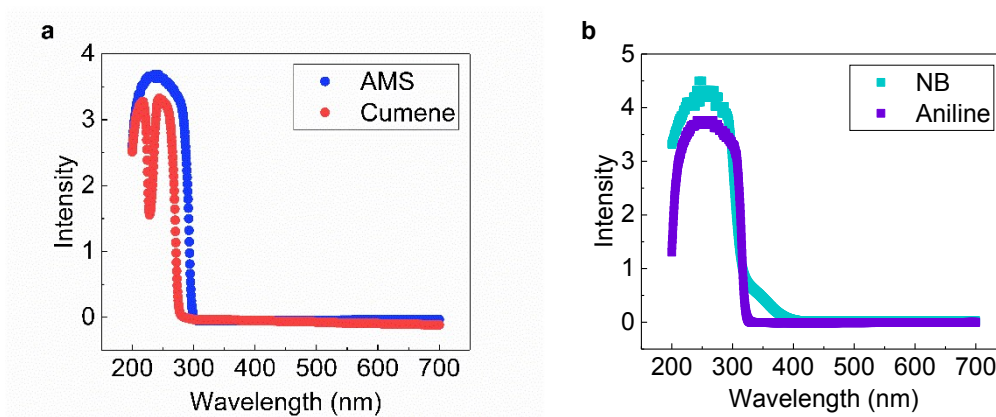
Fig S2. UV-vis spectra of (a) AMS, Cumene and (b) NB, aniline. Operation conditions: (a) Mass fraction: 1wt%; (b) Mass fraction: 0.015wt% (NB), 0.012wt% (Aniline); solvent: methanol.

3. Calculation of internal diffusion

In order to determine the effect of internal mass transfer, Thiele modulus was calculated by using equation (S1, S2, S3) and efficiency factors were obtained through the equation (S4):

$$D_m = 7.4 \times 10^{-8} \left[\frac{(\varphi M_2)^{0.5} T}{\mu_1 V_1^{0.6}} \right] \#(S1)$$

$$D_{eff} = D_m \frac{\varepsilon}{tortuoxity} \#(S2)$$

$$\phi = L \sqrt{\frac{k'''}{D_{eff}}} \#(S3)$$

$$\eta = \frac{3}{\phi} \left(\frac{1}{tanh\phi} - \frac{1}{\phi} \right) \#(S4)$$

The values supporting this calculation are summarized in Table S2 and Table S3.

Table S2 Values of symbols in internal diffusion of α-methylstyrene.

Symbols	Significance	Value
φ	"Association parameter" for the solvent	1.0 [1]
M_2	Molecular weight of solvent (methanol)	32.04 g/mol
T	Temperature	299.15 K
μ_1	Viscosity of solvent (methanol)	0.94 mPa·s[2]
V_1	Molar volume of solute at its normal boiling point	14.3 for H_2[3] 76.5 for AMS[3]
ε	*Porosity*	0.38[1]
	Tortuoxity	2.7[1]
L	Characteristic length of catalyst particles (L=R/3 for sphere)	0.16 mm
k'''	Apparent reaction rate constant	0.7953 min^{-1}
$D_m(H_2)$	Molecular diffusion coefficient of H_2	$4.6 \times 10^{-9} m/s$

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$D_m(AMS)$	Molecular diffusion coefficient of AMS	$1.2 \times 10^{-9}\ m/s$
$D_{eff}(H_2)$	Effective diffusion coefficient of H_2	$6.5 \times 10^{-10}\ m/s$
$D_{eff}(AMS)$	Effective diffusion coefficient of AMS	$1.7 \times 10^{-10}\ m/s$
$\phi(H_2)$	Thiele modulus of H_2	0.295
$\phi(AMS)$	Thiele modulus of AMS	0.578
$\eta(H_2)$	Efficiency factor of H_2	0.994
$\eta(AMS)$	Efficiency factor of AMS	0.978

Table S3 Values of symbols in internal diffusion of nitrobenzene

Symbols	Meaning	Value
φ	"Association parameter" for the solvent	1.0[1]
M_2	Molecular weight of solvent (methanol)	32.04 g/mol
T	Temperature	304.15 K
μ_1	Viscosity of solvent (methanol)	0.94 mPa·s[2]
V_1	Molar volume of solute at its normal boiling point	14.3 for H_2[3] 101.2 for NB[3]
ε	*Porosity*	0.38[1]
	Tortuoxity	2.7[1]
L	Characteristic length of catalyst particles (L=R/3 for sphere)	0.16 mm
k'''	Apparent reaction rate constant	2.3737 L·mol⁻¹·min⁻¹
$D_m(H_2)$	Molecular diffusion coefficient of H_2	$1.17 \times 10^{-9}\ m/s$
$D_m(NB)$	Molecular diffusion coefficient of NB	$4.62 \times 10^{-9}\ m/s$
$D_{eff}(H_2)$	Effective diffusion coefficient of H_2	$6.50 \times 10^{-10}\ m^2/s$
$D_{eff}(NB)$	Effective diffusion coefficient of NB	$2.01 \times 10^{-10}\ m^2/s$
$\phi(H_2)$	Thiele modulus of H_2	0.0328
$\phi(NB)$	Thiele modulus of NB	0.0590
$\eta(H_2)$	Efficiency factor of H_2	0.999
$\eta(NB)$	Efficiency factor of NB	0.999

4. Determination of residence time under flow rate ramping

The residence time, τ and a fluid element entering and exiting the reactor at time t_i and t_f, respectively. Time for the beginning of ramping is defined as 0 and time for the end of ramping is t_A and time reaching the reactor outlet correspond to t_A is $t_{f,A}$.

For $t_f < 0\,\text{min}$ $t_i < 0\,min$, saturated liquid flows through reactor with volume of V_r where bed porosity is ε at initial flow rate, Q_0.

$$\tau = \frac{\varepsilon V_r}{Q_0} \#(S5)$$

For $t_f > 0\,\text{min}$ $t_i < 0\,min$, integrating for the fluid element residence time as it travels the volume V_d between the end of reaction zone and the ultraviolet detector, and t_m is the time measurement occurs after fluid has flowed a volume V_d from the reactor outlet:

$$V_d = \int_{t_f}^{t_m} (Q_0 + at)dt \quad \#(S6)$$

From t_i to 0 min, saturated liquid flows through reactor at initial rate, Q_0. From 0 min to t_f, flow rate decreases constantly as $Q_0 + at$. Integrating for the fluid element residence time as it travels through the reactor volume:

$$\varepsilon V_r = \int_{t_i}^{0} Q_0 dt + \int_{0}^{t_f} (Q_0 + at)dt \quad \#(S7)$$

Solving two equations above, t_f, t_i and т could be expressed as follows:

$$t_f = \frac{Q_0 - \sqrt{Q_0^2 + 2a\left(\frac{a}{2}t_m^2 + Q_0 t_m - V_d\right)}}{-a} \#(S8)$$

$$t_i = \frac{Q_0 t_f + \frac{a}{2}t_f^2 - \varepsilon V_r}{Q_0} \#(S9)$$

$$\tau = t_f - t_i \#(S10)$$

For $t_m < t_A$ $t_f > 0\,min$ $t_i > 0min$, liquid flow rate flowing through reactor and volume between reaction zone and ultraviolet detector are both $Q_0 + at$. Two equations are obtained when the fluid element travels through V_r and V_d.

$$V_d = \int_{t_f}^{t_m} (Q_0 + at)dt \quad \#(S11)$$

$$\varepsilon V_r = \int_{t_i}^{t_f} (Q_0 + at)dt \#(S12)$$

Solving equations above, t_f, t_i and τ are obtained as:

$$t_f = \frac{Q_0 - \sqrt{Q_0^2 + 2a\left(\frac{a}{2}t_m^2 + Q_0 t_m - V_d\right)}}{-a} \#(S13)$$

$$t_i = \frac{Q_0 - \sqrt{Q_0^2 + 2a\left(\frac{a}{2}t_f^2 + Q_0 t_f - \varepsilon V_r\right)}}{-a} \#(S14)$$

$$\tau = t_f - t_i \#(S15)$$

For $t_m > t_A$ $t_f > 0\ min$ $t_i > 0min$, from t_f to t_A, flow rate flowing through V_d is $Q_0 + at$ from t_A to t_m, and the flow rate is constant as the final ramping flow rate, Q_A.

$$V_d = \int_{t_f}^{t_A} (Q_0 + at)dt + \int_{t_A}^{t_m} Q_A dt \#(S16)$$

From t_i to $t_{f,A}$, liquid flow rate flowing through V_r is $Q_0 + at$. From $t_{f,A}$ to t_f, flow rate is constant as the final ramping flow rate, Q_A.
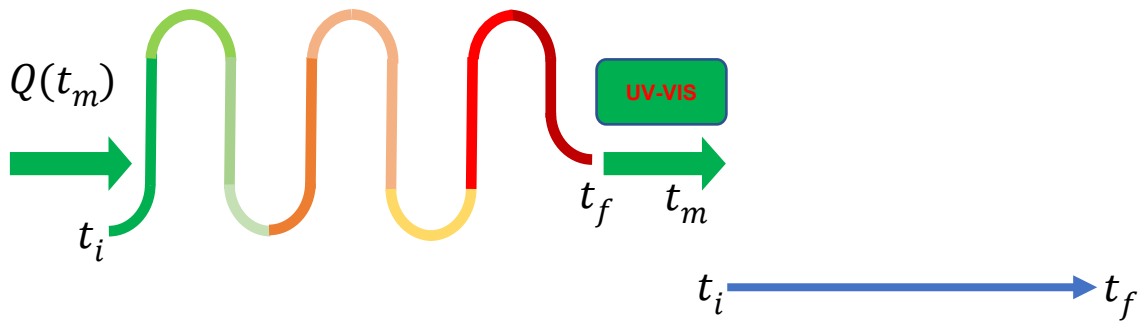
$$\varepsilon V_r = \int_{t_i}^{t_{f,A}} (Q_0 + at)dt + \int_{t_{f,A}}^{t_f} Q_A dt \#(S17)$$

Solving equation S16, S17, t_f, t_i and τ are obtained as:

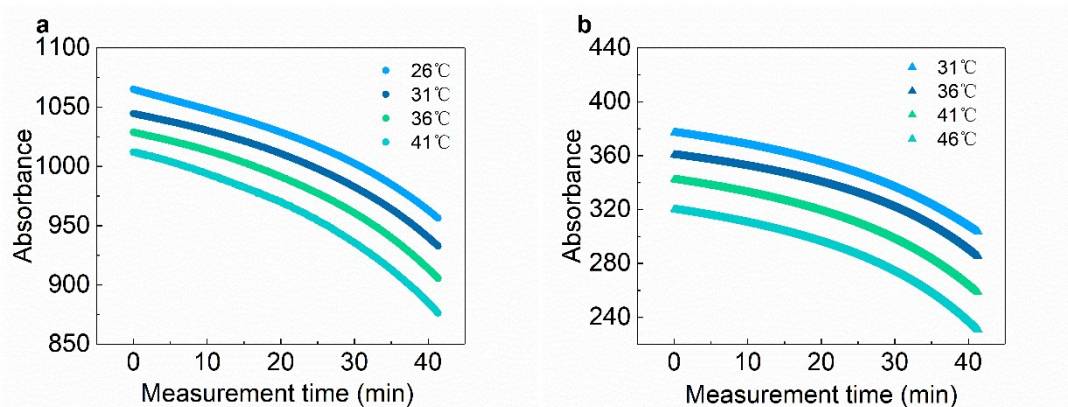$$t_f = \frac{Q_0 - \sqrt{Q_0^2 + 2a\left(Q_0 t_A + \frac{a}{2}t_A^2 + Q_A t_m - Q_A t_A - V_d\right)}}{-a} \#(S18)$$

$$t_i = \frac{Q_0 - \sqrt{Q_0^2 + 2a\left(Q_0 t_{f,A} + \frac{a}{2}t_{f,A}^2 + Q_A t_f - Q_A t_{f,A} - \varepsilon V_r\right)}}{-a} \#(S19)$$

$$\tau = t_f - t_i \#(S20)$$

Fig.S3 Representation of reaction in a low-dispersion flow reactor with ramping method. Color illustrates extent of conversion from low (green) to high (red).

5. Raw data of reaction kinetics at varied temperatures

Fig.S4 Absorbances of (a) α-methylstyrene and (b) nitrobenzene at different measurement times and temperatures. Reaction conditions: (a) α-Methylstyrene concentration: 0.06 mol/L, gas pressure: 1.0 MPa; (b) nitrobenzene concentration: 0.02 mol/L, gas pressure: 1.3 MPa; flow rate ramping: 0.02 mL/min/min, catalyst loading:5 wt%.
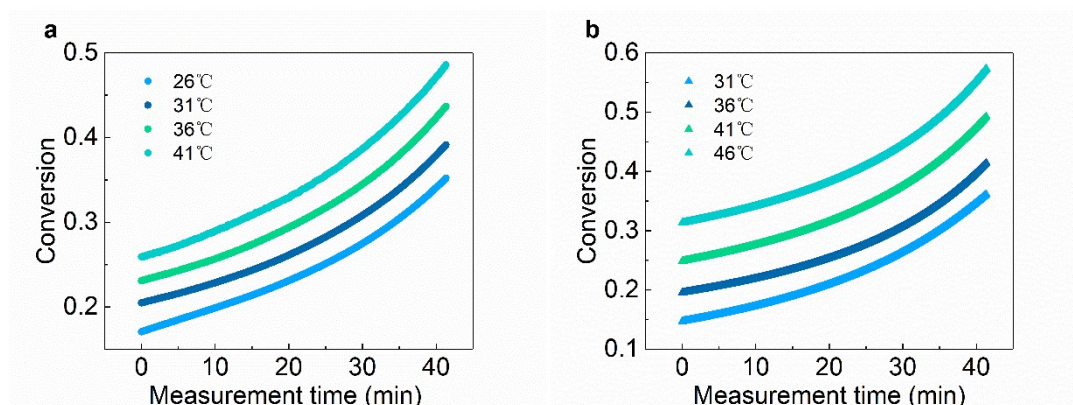
Fig.S5 Conversion of (a) α-methylstyrene and (b) nitrobenzene at different measurement times and temperatures. Reaction conditions: (a) α-Methylstyrene concentration: 0.06 mol/L, gas pressure: 1.0 MPa; (b) nitrobenzene concentration: 0.02 mol/L, gas pressure: 1.3 MPa; flow rate ramping: 0.02 mL/min/min, catalyst loading: 5 wt%.

6. Linear fitting results of reaction rate constants for α-methylstyrene and nitrobenzene

Table S4 Linear fitting results of reaction rate constants for α-methylstyrene

Temperature/℃	Curve fitting equation	R-square
26	y=24.403x	0.9993
31	y=28.268x	0.999
36	y=32.949x	0.9997
41	y=38.920x	0.9998

Table S5 Linear fitting results of reaction rate constants for nitrobenzene

Temperature/℃	Curve fitting equation	R-square
31	y=15.809x	0.9995
36	y=19.340x	0.9997
41	y=25.595x	0.9996
46	y=33.545x	0.9992

7. References

1. C. Yang, A. R. Teixeira, Y. Shi, S. C. Born, H. Lin, Y. L. Song, B. Martin, B. Schenkel, M. P. Lachegurabi and K. F. Jensen, *Green chemistry*, 2018, **20**, 886-893.
2. R. A. Lewis, *Hawley's condensed chemical dictionary*, John Wiley & Sons, 2016.

3. N. T. Program, *National Toxicology Program Chemical Repository Database. Research Triangle Park, North Carolina: NTP via httn. canieochemicals. noaa. gov/chemical/20568.*