Supporting Information

Alternating Magnetic Field Mediated Micro Reaction System for Palladium-Catalyzed Coupling Reactions

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S.1.The process of Villermaux-Dushman reaction

Villermaux-Dushman reaction is competitive iodide/iodate reaction. This reaction is used in study to evaluate the mixing performance of the reactor.

$H_2BO_3^- + H^+ \rightarrow H_3BO_3$ quasi-instantaneous (R1)

$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ very fast (R2)

$I_2 + I^- \leftrightarrow I_3^-$ quasi-instantaneous (R3)

Because the reaction (R1) is quasi-instantaneous, excessive $H_2BO_3^-$ in solution consume H^+ quickly. However, the zone existed locally excessiveH^+ may contact with iodide and iodate ions. Iodine made in this Redox reaction (R2) is reacted with iodide ions and makes tri-iodide ions by (R3). The tri-iodide ion under ultraviolet light shows absorption peaks at 353nm wavelength. Thus, concentration of tri-iodide ions could be decided quantitatively by spectrophotometer, we can confirm the mixing performance of the reactor.

Kinetics for each reaction can be described as

$$r_1 = k_1 C_{H^+} C_{H_2BO_3^-}$$

$$r_2 = k_2 C_{H^+}^2 C_{I^-}^2 C_{IO_3^-}$$

$$r_3 = k_{3+} C_{I^-} C_{I_2} - k_{3-} C_{I_3^-}$$

The equilibrium constant of iodine/iodide/tri-iodide is defined by K_{eq}. As concentrations of species are stopped changing,

$$K_{eq} = \frac{C_{I_3^-}}{C_{I_2} C_{I^-}} \tag{1}$$

D.A. Palmer gives[1]

$$log_{10}K_{eq} = \frac{555}{T} + 7.355 - 2.575 log_{10}T \tag{2}$$

T is temperature. From this equation, we can relate the equilibrium constant with reaction temperature.

Using Beer-Lambert Law, we can calculate the tri-iodide ions.

$$C_{I_3^-} = \frac{O.D.}{\epsilon_{353} \cdot l} \tag{3}$$

O.D. is the optical density measured by spectrophotometer and $l = 1cm$, which is the optical path length, thickness of the cuvette. Extinction coefficient for tri-iodide ions at 353nm, ϵ_{353} is 26047L/(mol cm).

Segregation index(X_s) to figured the mixing performance is defined by Eq.(4)

$$X_s = \frac{Y}{Y_{ST}} \tag{4}$$

The produced iodine means the amount of consumption of acid during reaction. Segregation index ranges from 0 to 1, where $X_s = 0$ means perfect mixing and $X_s = 1$ means that two fluids are entirely segregated. Y is the ration of consumption of acid by (R2) to the whole consumption of acid by (R1) and (R2), and Y_{ST} is the assumed value of Y having total segregation.

Table 1. Concentration of solutions used in Villermaux-Dushman reaction to test mixing performance

	Concentration [mol/L]
Solution 1	
H_2SO_4	0.0025
Solution 2	
$NaOH$	0.0045

H_3BO_3	0.0045
KI	0.0015
KIO_3	0.0003

For total segregation, all iodate ions would be consumed by (R2). Y_{ST} can be calculated as:

$$Y_{ST} = \frac{6n_{IO_3^-,0}}{6n_{IO_3^-,0} + n_{H_2BO_3^-,0}} = \frac{6C_{IO_3^-,0}}{6C_{IO_3^-,0} + C_{H_2BO_3^-,0}} \tag{5}$$

Where n is molar number, C is the concentration, subscript 0 means concentrations of initial values. Y is calculated with the ratio of acid consumed to produce iodine, with total hydrogen ions from sulfuric acid. Tri-iodide ions should be considered together with iodine.

$$Y = \frac{2(n_{I_2} + n_{I_3^-})}{n_{H_0^+}} = \frac{2(C_{I_2} + C_{I_3^-})}{C_{H_2SO_4}} \tag{6}$$

Now, consider mass balance of iodine of the (R2). This can be written as:

$$n_{I^-} = n_{I^-,0} - \frac{5}{3}\left(n_{I_2} + n_{I_3^-}\right) - n_{I_3^-} \tag{7}$$

Where $n_{I^-,0}$ is the initial mole of iodide in solution 2. Eq.(7) is modified to final equation Eq.(8)

$$C_{I^-} = \frac{C_{I^-,0}}{2} - \frac{5}{3}\left(C_{I_2} + C_{I_3^-}\right) - C_{I_3^-} \tag{8}$$

We can combine the equilibrium equation Eq.(1) and the mass balance equation (8) to measure concentration of iodine/tri-iodide.

$$-\frac{5}{3}C_{I_2}^2 + \left(\frac{C_{I^-,0}}{2} - \frac{8}{3}C_{I_3^-}\right)C_{I_2} - \frac{C_{I_3^-}}{K_{eq}} = 0 \tag{9}$$

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[1] DA. Plamer, R.W. Ramette and R.E. Mesmer, *J. Sol. Chem.*, 1984, 13, 673.

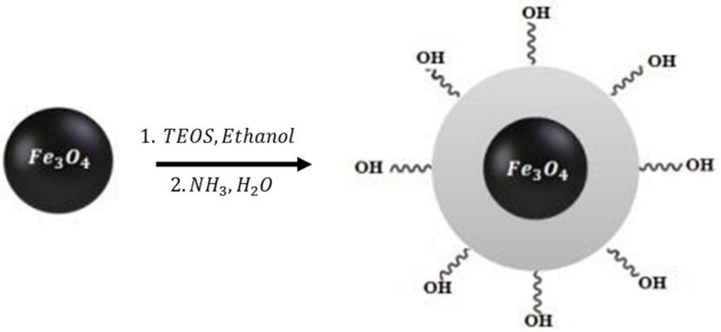
The segregation index X_s could be calculated by Eqs. (4), (5) and (6).

Mixcromixedness ratio, α is also indicator that can be used to confirm the mixing efficiency. Mixcromixedness ratio α can be defined as the ratio of a perfectly mixed volume to the totally segregated volume.

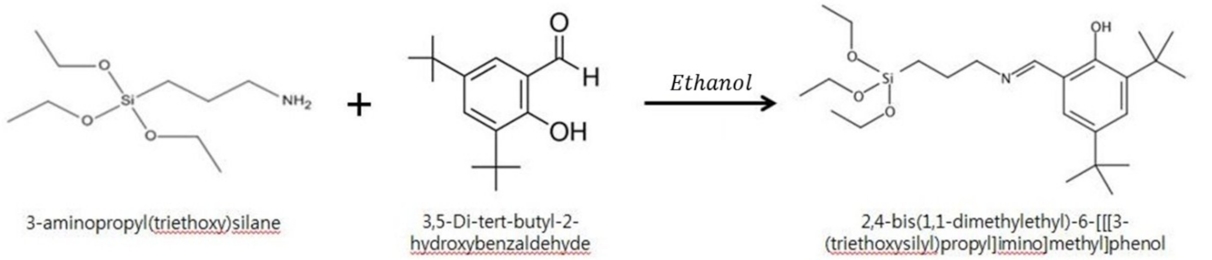
$$\alpha = \frac{1}{X_s} - 1 \tag{10}$$

The higher value of the α, the better mixing efficiency.

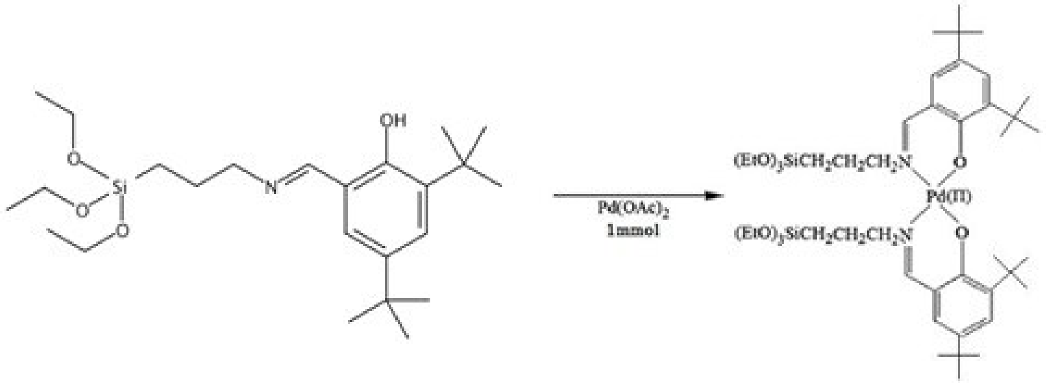
S. 2. The synthetic procedure of catalytic magnetic particles



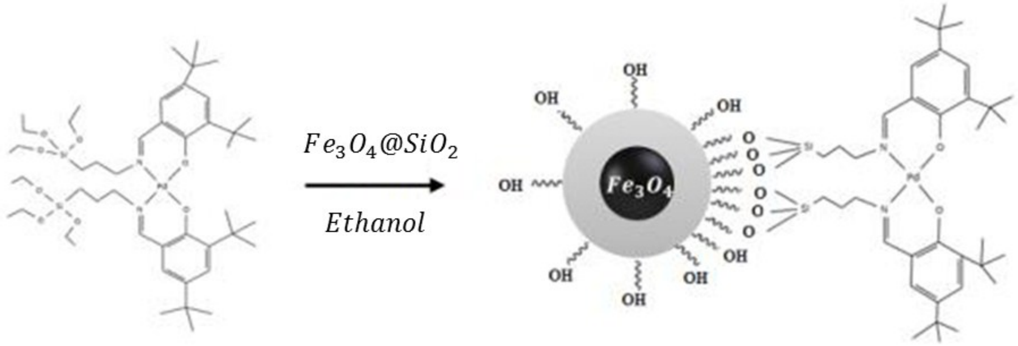
Using modified Stober method, we made $Fe_3O_4@SiO_2$ particles. Fe_3O_4 particles were purchased from Aldrich and Alfa Aesar in different size. First, Fe_3O_4(0.02g) and tetraethyl orthosilicate(2ml) were stirred in ethanol solution (6ml) at r.t. for 2days. Ammonia(1ml) and deionized water(0.5ml) were added in the solution. Solution was stirred continuously at r.t. for 3days. The product was washed with deionized and ethanol several times and dried in vacuum oven.



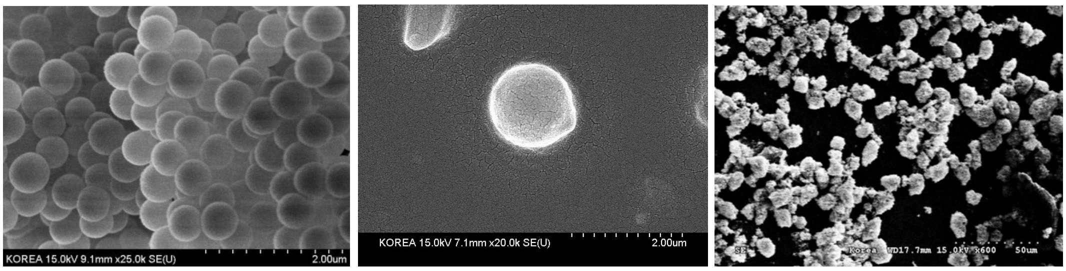
Next, we prepared Schiff base complex of palladium. 3-aminopropyl(triethoxy)silane (2mmol) in 40ml ethanol and 3,5-Di-tert-butyl-2-hydroxybenzaldehyde (2mmol) in 40ml ethanol were mixed and stirred at r.t. for 6h. After separating, product Schiff base was washed with ethanol and dried in vacuum oven. Palladium acetates (1mmol) was added to the solution of Schiff base (2mmol) in 25ml ethanol. This mixture was refluxed at 80℃ for 24h. The product was filtered and washed with ethanol several times.



Lastly, $Fe_3O_4@SiO_2$ (2g) was added in the solution of Schiff base/Pd in 25ml ethanol. This mixture was refluxed at 80℃ for 24h. The remaining solid was separated by external permanent magnet and washed with ethanol and acetone several times. The product was dried at 80℃ for 12h.



S3. SEM Image of catalyst



(a) 0.3μm (b) 1μm (c) 15μm