



## SUPPLEMENTARY INFORMATION

### Characterization methodology

Different characterization techniques were employed to characterize the fresh and used catalyst. The details are given here:

The surface area was calculated by using BET N<sub>2</sub> adsorption method on ASAP 2010 instrument (Micromeritics, USA).

The X-ray powder diffraction (XRD) patterns of prepared samples were collected on a diffractometer (Bruker AXS, D8 Discover instrument) using Cu K $\alpha$  radiation (1.5406 Å) at 40kV and 100 mA with step scanning in the 2 $\theta$  range of 5-80° with stepping time of 0.5 s.

A Perkin Elmer instrument was used to collect the FT-IR spectra of different samples. The sample were prepared by using KBr and sample in approximately 100:1 (weight ratio) and transformed in pellets by using high pressure instrument. The wave number range was set from 4000 to 400cm<sup>-1</sup>.

An Autochem II 2920 (Micromeritics, USA) instrument was employed to obtain the ammonia TPD of different samples. Around 30 mg of catalyst under study was pre-treated at 300°C under helium as carrier gas in a quartz U-tube micro reactor for 1 h. Thereafter the temperature was brought down to 50°C and 10% NH<sub>3</sub> in helium was flown for 30 min at the flow rate of 50 ml/ min. Physisorbed NH<sub>3</sub> was flushed out by the helium at 50°C for 30 min before starting the desorption experiments. The TPD of ammonia was recorded by heating the sample from 50°C to 650°C at a rate of 30°C/min under the pure helium flow set at 50 ml /min.

TGA analysis of different samples were done on NETSCH instrument by using appropriate amount of samples under nitrogen atmosphere from temperature range of 30°C to 650°C with scan rate of 30 °C/min.

The external morphology of samples was recorded by using SEM image collected on JEOL-JSM-6380 LA (Japan) instrument.

### Proof of absence of mass transfer or diffusion resistance

For a liquid-solid catalytic reaction different mechanism has been proposed. To get insight to the role of mass transfer resistance, the diffusivity of diphenyl oxide and benzoic anhydride were evaluated at reaction temperature of 130°C by using Wilke-Chang equation.<sup>1</sup> The diffusivities of respective reactant were found to be D<sub>BD</sub> (diffusivity of benzoic anhydride) as 0.38 x 10<sup>-5</sup>cm<sup>2</sup>/s and D<sub>DB</sub> (diffusivity of diphenyl oxide) as 0.77x 10<sup>-5</sup>cm<sup>2</sup>/s. The mass transfer coefficients  $k_{SL-B}$  and  $k_{SL-D}$  were evaluated by using these diffusivities value by considering the Sherwood number as 2<sup>2-4</sup> and found to be 1.26 x 10<sup>-3</sup>cm/s and 2.56 x10<sup>-3</sup>cm/s respectively. Further the particle surface area per liquid volume for spherical particle can be calculated as:

$$a_p = \frac{6W}{\rho_p d_p} = 43.65 \text{ cm}^2/\text{cm}^3 \quad (1)$$

The mass transfer rate of the reactants was calculated by using equation 2 and 3:

$$R_B = k_{SL-B} a_p [B_0 - B_s] \quad (2)$$

$$R_D = k_{SL-D} a_p [D_0 - D_s] \quad (3)$$

The speed of agitation study confirms that there is no mass transfer resistance for both reactant from bulk to catalyst surface hence B<sub>0</sub> and D<sub>0</sub> are same as that of B<sub>s</sub> and D<sub>s</sub>. Hence from equation 2 and 3, the mass transfer rates were calculated as  $R_B = 7.1 \times 10^{-4} \text{ mol/ (cm}^3\text{s)}$  and  $R_D = 2.87 \times 10^{-4} \text{ mol/ (cm}^3\text{s)}$ . The observed initial rate of benzylation of diphenyl oxide ( $r_{\text{obs}}$ ) was

found to be  $1.4 \times 10^{-7} \text{ mol}/(\text{cm}^3\text{s})$ . Thus, the mass transfer rates are very high in comparison of the reaction rate which confirms that there is no effect of external mass transfer resistance at and beyond 800 rpm.

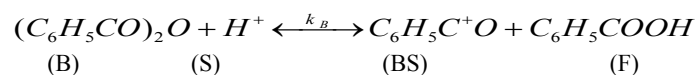
### Proof of absence of intra-particle resistance

By taking the average particle size of  $\text{Al}_{0.66}\text{-DTP/K-10}$  as 0.006 cm, a theoretical computation was done by invoking the Weitz-Prater modulus ( $C_{wp}$ ) in order to see the influence of intra particle resistance on rate of benzylation. <sup>5</sup> The details related to these can be easily found in some of our published literature. <sup>4, 6</sup> In present reaction, the  $C_{wp}$  value was found to be  $2.26 \times 10^{-3}$  which is very less than unity and hence there is no role of intra-particle diffusion resistance on the overall rate of reaction. Hence the reaction is supposed to be kinetically controlled which was confirmed by the activation energy calculation.

### Development of Theoretical Model

A detailed kinetic model was developed by using various studies as done above. The Eley-Rideal mechanism was supposed to be the best suited model based on the preliminary analysis. Consider D (diphenyl oxide), B (benzoic anhydride), product E (4-phenoxybenzophenone) and F (co-product benzoic acid).

The first step involves the benzoic anhydride (B) adsorption on a catalytic site (S):



The rate of chemisorptions of B:

$$-r_B = k_B C_B C_S - k'_B C_{BS} C_F \quad (1)$$

$$-r_B = 0 \text{ at equilibrium}$$

$$k_B C_B C_S = k'_B C_{BS} C_F \quad (2)$$

$$\text{Since } K_B = \frac{k_B}{k'_B}$$

$$C_{BS} = K_B \frac{C_B C_S}{C_F} \quad (3)$$

$$-\ln(1 - X_B) - [K_B(M-1) - M] \ln \left[ \frac{M - X_B}{M} \right] = [kK_B(M-1)wt] \quad \text{The}$$

reaction between chemisorbed BS and D takes place as follows:



Considering, the surface reaction between the chemisorbed BS and reactant D as rate limiting step. The rate of benzylation of diphenyl oxide based on the conversion of benzoic anhydride B is given as:

$$-\frac{dC_B}{dt} = kC_D C_{BS} \quad (4)$$

Substituting  $C_{BS}$  in above equation,

$$-\frac{dC_B}{dt} = kC_D \frac{K_B C_B C_S}{C_F} = kK_B \frac{C_D C_B C_S}{C_F} \quad (5)$$

The total catalytic site balance can be written as ,

$$C_t = w = C_{BS} + C_S \quad (6)$$

Considering,  $w = C_{BS} + C_S$

$$C_S = \left( \frac{w}{1 + K_B C_B / C_F} \right) \quad (7)$$

After substituting the value of  $C_S$  in Eq. (5),

$$-\frac{dC_B}{dt} = \frac{kK_B w C_D C_B}{(C_F + K_B C_B)} = r_D = r_B \quad (8)$$

$$C_B = C_{B_0} (1 - X_B) \quad (8a)$$

$$C_D = C_{D_0} - C_{B_0} X_B = C_{B_0} (M - X_B) \quad (8b)$$

$$C_F = C_{B_0} X_B \quad (8c)$$

Substituting in terms of  $X_B$  and integrating the Equation 8 with  $M \neq 1$ , we get

$$(9)$$

Using Polymath 6.0 Software various constants were calculated by using temperature data and the results are presented in Table 5.

## NOMENCLATURE

$a_p$	surface area per unit liquid volume, $\text{cm}^2/\text{cm}^3$
B	reactant species B, benzoic anhydride
$B_0$	concentration of B in bulk liquid phase, $(\text{mol}/\text{cm}^3)$
$B_S$	Chemisorbed B
$C_B$	concentration of B, $(\text{mol}/\text{cm}^3)$
$C_D$	concentration of D, $(\text{mol}/\text{cm}^3)$
$C_F$	concentration of F in, $(\text{mol}/\text{cm}^3)$
$C_{wp}$	Weisz Prater parameter
$d_p$	diameter of catalyst particle, $(\text{cm})$
D	reactant species D, Diphenyl oxide
$D_0$	concentration of D in bulk liquid phase, $(\text{mol}/\text{cm}^3)$
$D_{BD}$	diffusion coefficient of B in D, $(\text{cm}^2/\text{s})$
$D_{DB}$	diffusion coefficient of D in B, $(\text{cm}^2/\text{s})$
$D_e$	effective diffusivity, $(\text{cm}^2/\text{s})$
E	4-Phenoxybenzophenone
F	benzoic acid
k	reaction rate constant $(\text{cm}^6\text{mol}^{-1}\text{g}^{-1}\text{s}^{-1})$
$k_{SL-B}, k_{SL-D}$	solid-liquid mass transfer coefficients, $(\text{cm}/\text{s})$
$K_B$	adsorption equilibrium constant for B $(\text{cm}^3/\text{mol})$
M	mole ratio of A to B
$r_{obs}$	observed rate of reaction based on liquid phase volume $(\text{mol}/\text{cm}^3 \text{ s})$
$R_B$	rate of mass transfer of species B into liquid phase $(\text{mol}/\text{cm}^3 \text{ s})$
$R_D$	rate of mass transfer of species D into liquid phase $(\text{mol}/\text{cm}^3 \text{ s})$
w	catalyst loading $(\text{g}/\text{cm}^3)$
$X_B$	fractional conversion of B

## REFERENCES

- [1] R.C. Reid, M.J. Prausnitz, T.K. Sherwood, *The Properties of Gases and Liquids*, 3<sup>rd</sup> ed. McGraw-Hill, New York, 1977.
- [2] G.D. Yadav, N. Kirthivasan, *Appl. Catal. A: Gen.* 154 (1997) 29–53.
- [3] G.D. Yadav, N.S. Doshi, *Catal. Today* 60 (2000) 263–273.
- [4] M.S. Tiwari, G.D. Yadav, *Chem. Eng J.* 266 (2015) 64–73.
- [5] H.S. Fogler, *Elements of Chemical Reaction Engineering*, 2<sup>nd</sup> ed. Prentice-Hall, New Delhi, India. 1995.
- [6] G.D. Yadav, H.G. Manyar, *Micropor. Mesopor. Mater.* 63 (2003) 85–96.