Supporting information

Liquid phase Claisen-Schmidt condensation biomass derived furufraldehyde with acetophenone over solid super base catalyst

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Effect of various parameters:

Effect of speed of agitation

The understand the influence of mass transfer resistance on the rate of reaction, speed of agitation was studied from 600 to 1200 rpm at 120 °C at a catalyst loading of 0.0127 g/cm^3. The conversion increased from 600 to 1000 rpm beyond which the conversion and product distribution was practically similar (Figure 1). Thus, external resistance to mass transfer was absent beyond 1000 rpm. However, to be on safer side and to avoid abrasion of the catalyst, further experiments were conducted at 1000 rpm. We have discussed the theoretical development in some of our earlier publications. The influence of external solid-liquid mass transfer resistance must be ascertained before true kinetic model could be developed.
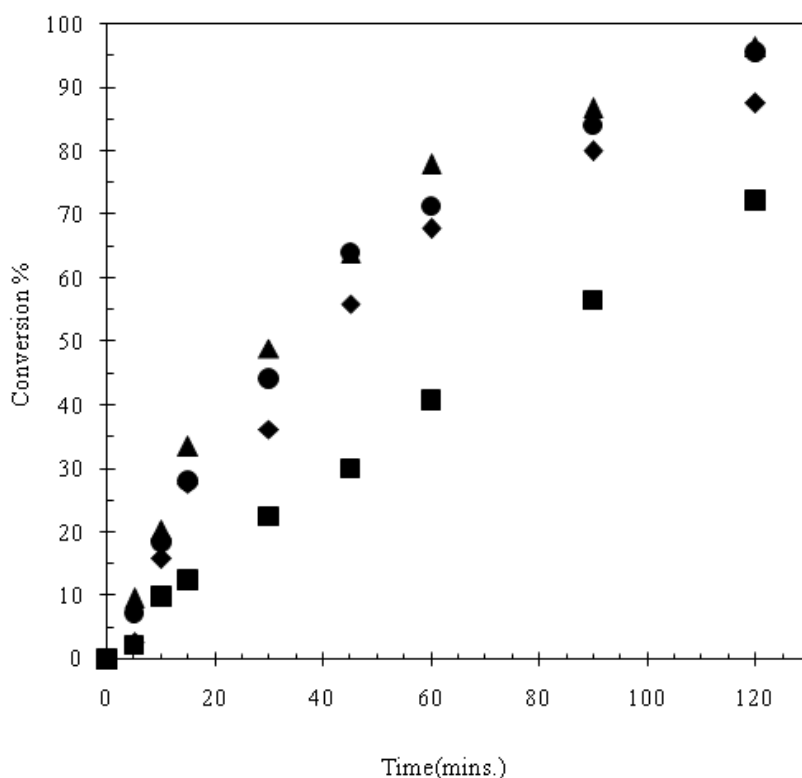

Fig. S 1 Effect of speed of agitation

Reaction condition: Catalyst: 15% w/w Al$_2$O$_3$/CaO, Furfuraldehyde-0.01 mol, Acetophenone-0.02 mol, Catalyst loading 0.012 g/cm^3, SOA-1000 rpm, Temperature -120 °C, solvent-Ethanol, Internal standard-n-Decane-200 μL, ■ 600 rpm, ◆ 800rpm, ● 1000rpm, ▲1200 rpm.

Effect of catalyst loading

In absence of mass transfer resistance and intra-particle diffusion resistance, the rate of reaction is directly proportional to the catalyst loading based on the total reaction volume, which was varied from 0.0081 to 0.015 g/cm^3 keeping the mole ratio at 1:2. Both the rate of reaction and conversion had
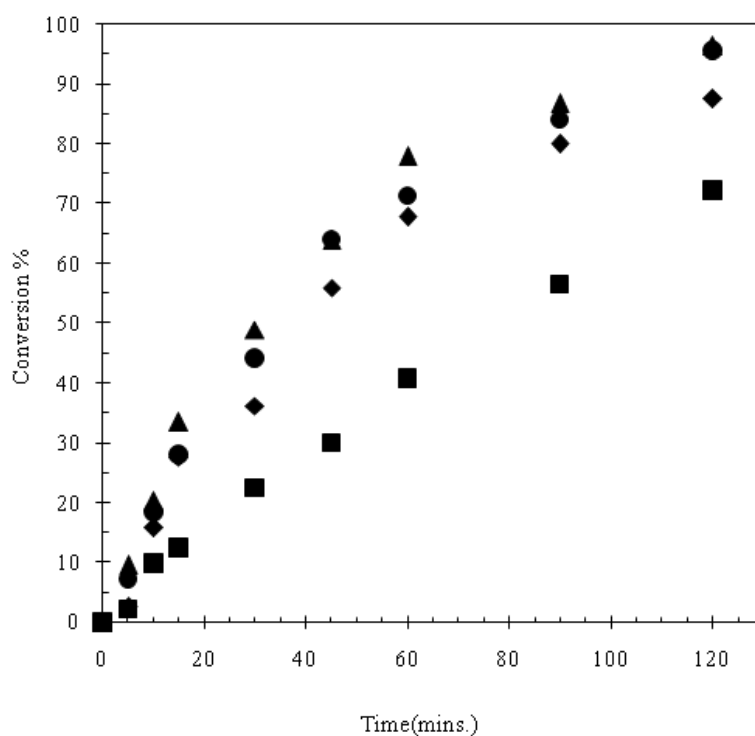

Fig. S 2 Effect of catalyst loading

Reaction condition: Catalyst: 15% w/w Al_2O_3/CaO, Furfuraldehyde-0.01 mol, Acetophenone-0.02 mol, Catalyst loading 0.012 g/cm^3, SOA-1000 rpm, Temperature -120 °C, solvent-Ethanol, Internal standard-n-Decane-200 μL, ■ 0.0081g/cm^3, ◆ 0.01g/cm^3, ● 0.0127g/cm^3, ▲0.015g/cm^3.

increased for catalyst loading up to 0.0127 g/cm^3 due to proportional increase in active sites available for the reaction (Figure 2). The rate of reaction was almost the same for catalyst loading of 0.0127 to 0.015 g/cm^3 and yield of 95.6% was obtained in both the cases. This can be explained that beyond a certain catalyst loading, there existed an excess number of catalyst sites than actually required by the reactant molecules. Hence, further study was conducted at catalyst loading of 0.0127 g/cm^3.

Effect of mole ratio

The mole ratio of furfuraldehyde to acetophenone was assorted from 1:1 to 1:3 with optimum catalyst loading of 0.0127 g/cm^3 at 120 °C (Figure 3). It was observed that the initial rate of the reaction increased with increase in mole ratio and beyond a mole ratio 1:2, there was no effect. Hence further all reactions were carried out at mole ratio of 1:2 of furfuraldehyde with acetophenone.
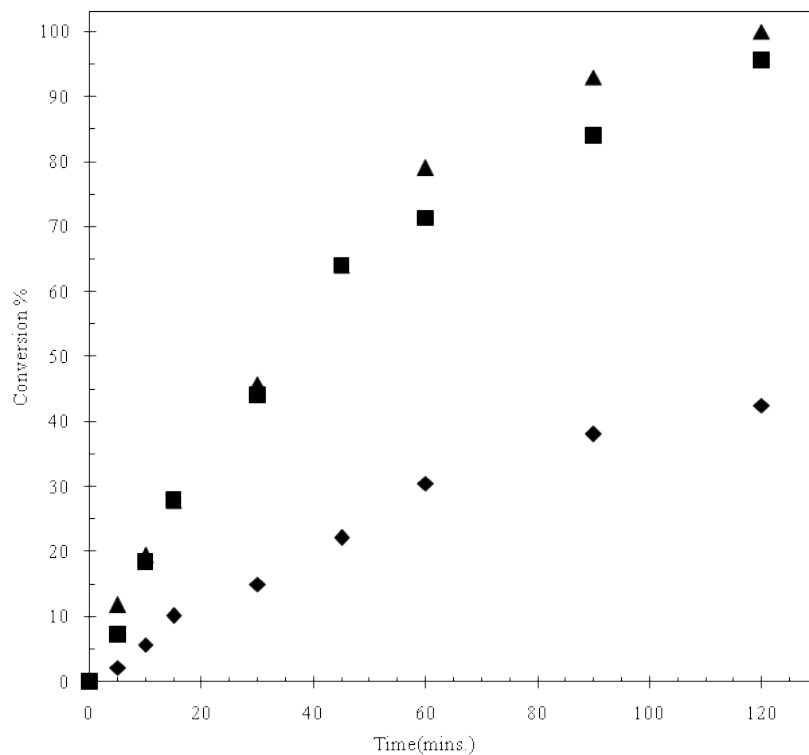
Fig. S 3 Effect of mole ratio

Reaction condition: Catalyst: 15% w/w Al_2O_3/CaO, Furfuraldehyde-0.01 mol, Acetophenone-0.02 mol, Catalyst loading 0.012 g/cm^3, SOA-1000 rpm, Temperature -120 °C, solvent-Ethanol, Internal standard-n-Decane-200 µL, ◆1:1, ■ 1:2, ▲ 1:3.

Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the range of 100 ℃ to 130 ℃ (Figure 4). It was observed that the conversion increases with increase in temperature, suggesting a kinetically controlled reaction which will be discussed later.
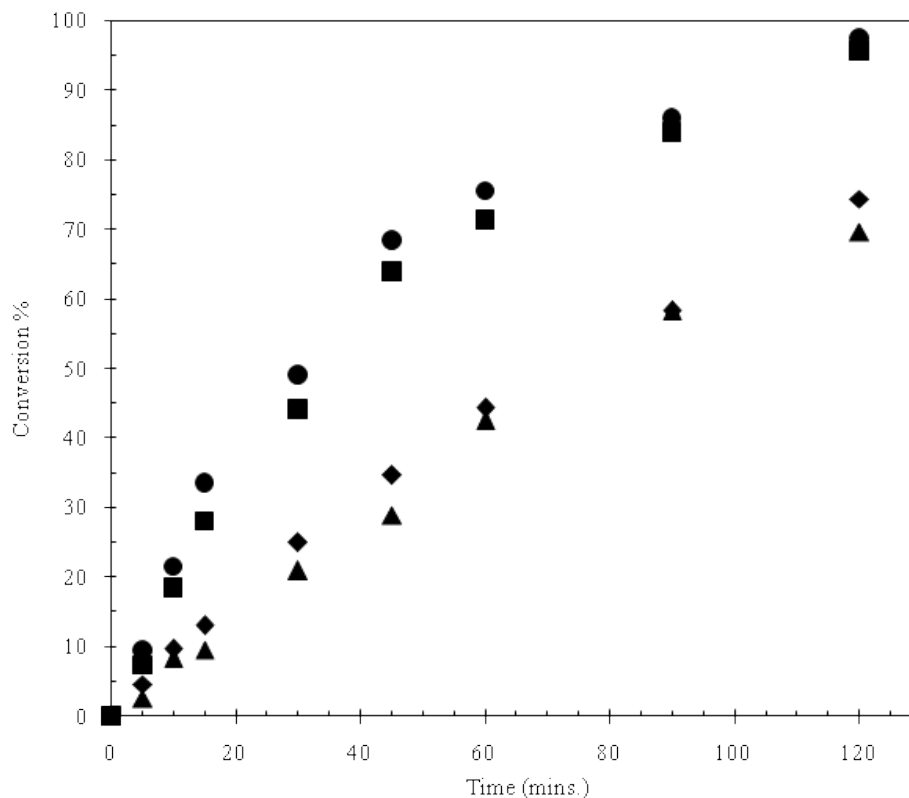
Fig. S 4 Effect of temperature

Reaction condition: Catalyst: 15% w/w Al_2O_3/CaO, Furfuraldehyde-0.01 mol, Acetophenone-0.02 mol, Catalyst loading 0.012 g/cm³, SOA-1000 rpm, Temperature -120 °C, solvent-Ethanol, Internal standard-n-Decane-200 μL, ▲ 100 °C, ◆ 110 °C, ■ 120 °C , ● 130 °C.

Proposed reaction mechanism

The synergistic effect of acidic and basic sites present in the catalyst helps to understand the path of formation of product. The mechanism of product formation after the reaction of furfuraldehyde with acetophenone using 15% w/w Al_2O_3/CaO is depicted in Scheme 1.
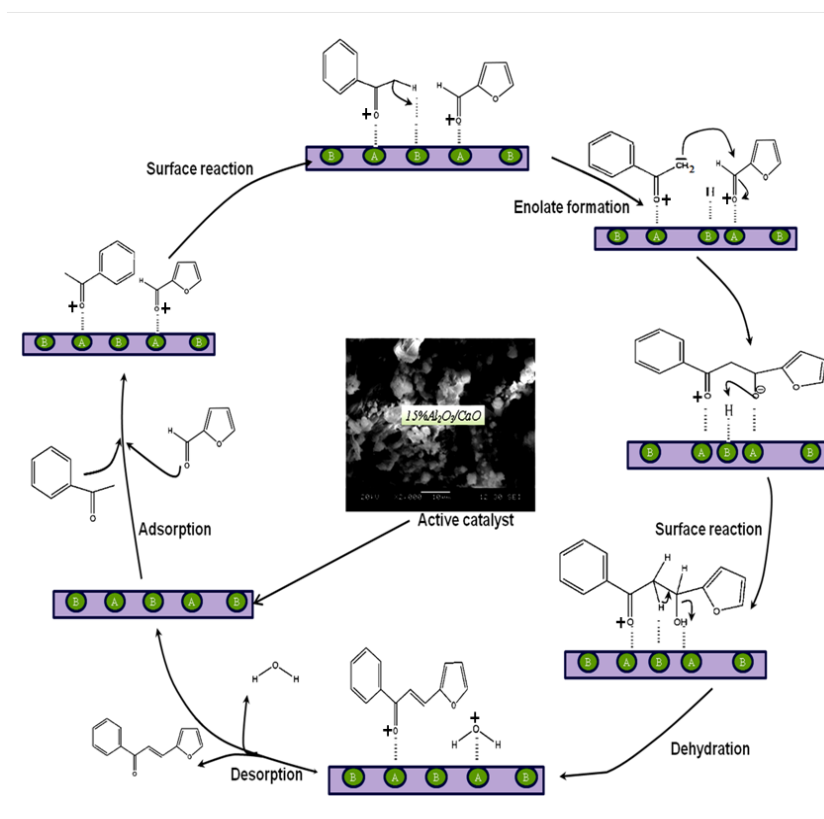
Scheme S 1. Proposed reaction mechanism on catalyst surface

First of all acetophenone is exclusively activated by deprotanation of α-carbon atom by the basic site on the surface of catalyst to give reactive carbanion i.e. enolate. At the same time the oxygen of furfuraldehyde is activated by co-ordination with Lewis acidic site of the catalyst, which leads to polarization of that group. Now the carbonyl carbon of furfuraldehyde is more susceptible for the attack by enolate anion of the acetophenone formed at the adjacent site. The intermediate alkoxide so formed takes proton from the medium to give β-hydroxy ketone. The presence of acidic and basic sites in the vicinity of each other helps in dehydration of β-hydroxy ketone to give the desired product.

Development of mechanistic model and kinetics of the reaction

In the absence of both external mass transfer and intraparticle diffusion resistances, the reaction could be controlled by one of the following steps, namely adsorption, surface reaction or desorption. The initial rate data were analyzed on the basis of Langmuir-Hinshelwood-Hougen-Watson (LHHW) type of mechanism.

When all species are weakly adsorbed, the rate equation becomes a power law model which could be integrated as follows:

$$\ln\left[\frac{(M - X_A)}{M(1 - X_A)}\right] = k_1 C_{A_0}(M - 1)t$$

(1)

A plot of $\ln\left[\dfrac{(M - X_A)}{M(1 - X_A)}\right]$ against t was made at different temperatures (Figure 5). The model fits very well. The apparent energy of activation was calculated by plotting Arrhenius plot as 12.5 kcal/mol (Figure 6).
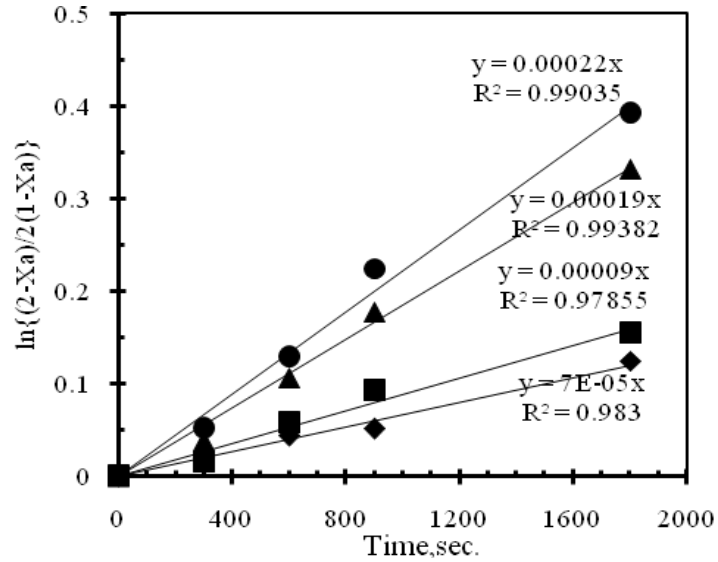

Fig. S 5 Second order kinetic plot

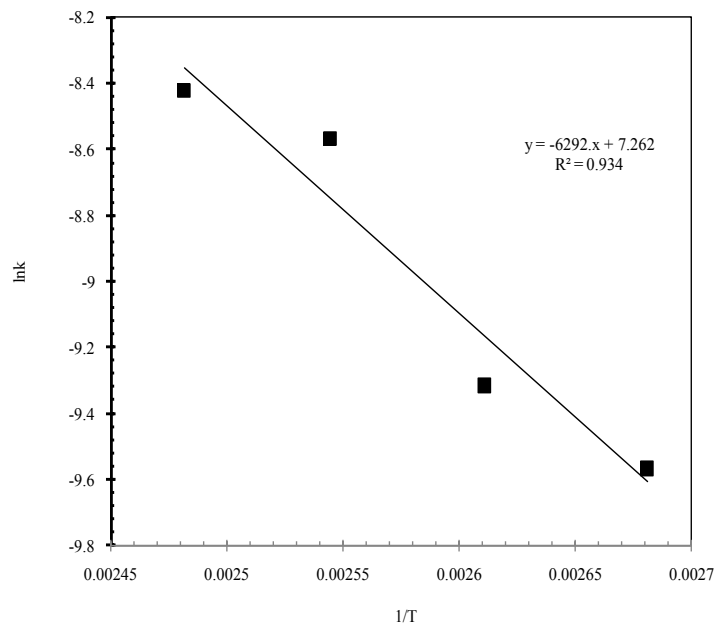Temperature: ◆100 °C, ■110 °C, ▲120 °C , ●130 °C.

Fig. S 6 Arrhenius plot