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Novelty of Claisen-Schmidt condensation of biomass-derived furfural with acetophenone over solid super base catalyst

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Valorization of biomass into value added chemicals and products using green technologies have been a subject matter of several papers. Claisen-Schmidt condensation of furfural with acetophenone to produce α, β-unsaturated keto compound, 3-(furan-2-yl)-1-phenylprop-2-en-1-one, is commercially attractive since it is used in pharmaceutical industry and can be hydrogenated to give high quality diesel fuel. In the current work, preparation and characterization of 5-15% w/w Al_2O_3 on CaO was done using FT-IR, TGA, XRD, SEM, EDXS, TPD and nitrogen BET. It was used in the reaction of furfural with acetophenone and its activity and selectivity were compared with other catalysts in a batch reactor at 120 °C. 15% w/w Al_2O_3/CaO was the best catalyst. It was 100% selective towards the formation of 3-(furan-2-yl)-1-phenylprop-2-en-1-one. The catalyst is robust and can be reused without loss of activity. The kinetics of the reaction follows Langmuir-Hinshelwood-Hougen-Watson mechanism with weak adsorption of all species leading to typical second order kinetics. The apparent energy of activation is 12.5 kcal/mol.

Introduction

Chalcones have diverse biological activities and possess antioxidant, antimicrobial, antimalarial, antileishmanial, anti-inflammatory, antitumor and antibacterial activity.[1-9] The existence of α, β-unsaturated keto function in chalcones is responsible for their antimicrobial activity, which may be altered depending on the nature and position of substituent on the aromatic ring.[3] Structure activity relationships of various alkoxylated and hydroxylated chalcones have been reported for antimalarial activity.[10] Chalcones bearing non-natural substituents have been synthesized during recent years and some derivatives find use as sweeteners, drugs, and sunscreen agents.[11] Traditionally, chalcones are synthesized via Claisen-Schmidt condensation using homogeneous basic catalysts such as NaOH, KOH and $Ca(OH)_2$. It is well known that such catalysts are beset with many drawbacks such as catalyst recovery, waste treatment and disposal resulting in high cost and a large E-factor.[12-15] As a potential alternative, heterogeneous catalysts have also been used for Claisen-Schmidt condensation, including Lewis acids, Brønsted acids, and solid bases.[16-24] These reactions have been used for the creation of a combinatorial library of chalcones.[25] Organolithium bases in apolar solvent were also used.[26] However, most of these methods require expensive reagents and toxic solvents to overcome heat and mass transfer problems in liquid phase reactions. Solid acid catalysts have been explored extensively for a variety of organic transformations, apart from their major bulk use in FCC in refineries, whereas limited efforts have been devoted towards development, characterization and application of solid base catalysts.[27-30] In terms of catalytic activity under mild and greener conditions, solid superbase catalysts are much superior to the conventional homogeneous catalysts. [31] Of late, increasing attention is focused on development of novel basic solid materials via different synthetic routes, which may be useful for several important base-catalyzed reactions.[32,33] Catalytic dehydration of sugar under ambient conditions gives furfural as one of the products, which is a precious platform molecule for manufacturing chemicals and fuels.[34] Hydrogenation of furfural gives linear C_5-C_6 adducts which have very poor performance as fuel.[35] The conversion of furfural into high quality fuel by aldol condensation with acetone followed by hydrogenation and deep hydrogenation was reported by Dumesic and co-workers.[36,37] As stated earlier, substantial information is available on homogeneous catalyzed synthesis of chalcones; but very few reports have disclosed activity of heterogeneous base catalysts for the said synthesis. Recently some papers have reported synthesis of furfural based chalcones by homogeneous route, which are not only inefficient but also brown processes.[38-42] As per our understanding there is no information on heterogeneous base catalyzed synthesis of furfural based chalcones. Recently our group has demonstrated activity and selectivity of calcined hydrotalcite supported on hexagonal mesoporous silica (CHT/HMS) in selectivity engineered base catalyzed reactions. [43,44] Herein for the first time, we report a simple and convenient method for preparation of solid super base and reusable catalyst for the synthesis of furfural based chalcones. Its performance is compared with several other catalysts to bring out its novelty. The catalyst was prepared by sol-gel method and thoroughly characterized by various analytical techniques such as FTIR, TPD, SEM, XRD, EDX, TGA and nitrogen BET pore analysis. Effects of various parameters affecting the reaction rate and conversions were investigated to deduce kinetics of the reaction. The overall process is clean and green.

Experimental

Chemicals

The following chemicals were procured from firms of repute and used without further purification. Calcium oxide, aluminium nitrate, magnesium nitrate, stronsium nitrate, acetophenone, furfural and decane were obtained from S.D. Fine Chemicals Ltd, Mumbai, India. The catalysts used for the reaction were dried at 120 ºC for 2 h before use. Calcined hydrotalcite (CHT) with different amount of magnesium loading, calcined hydrotalcite on HMS (CHT/HMS) and hydrated hydrotalcite (HHT) were prepared by well established procedures reported earlier by our laboratory.[43-45]

Catalyst Preparation

Al_2O_3/CaO catalyst was prepared by sol-gel method. The required amount of $Ca(OH)_2$ was dispersed in 250 cm^3 of water. Then 6.6227 g of Al $(NO_3)_3.9H_2O$ in 50 cm^3 of water was added drop wise in the above solution. After complete addition, the solution was stirred for 1 h and refluxed for 24 h at 120 °C. The solution was filtered and dried at 120 °C for 12 h and was subjected to calcination at 700 °C to get the desired catalyst. Thus, 5-15% w/w Al_2O_3/CaO was prepared by this method using appropriate quantities of the reagents. Similarly, 15% w/w Al_2O_3 supported on SrO and MgO were prepared.

HT(Hydrotalcite) was prepared by a standard procedure. A solution of 1 mol magnesium nitrate ($Mg(NO_3)_2.6H_2O$) and 0.5 mol aluminium nitrate ($Al(NO_3)_3.6H_2O$) was prepared by dissolving the corresponding salts in distilled water. The solution was then co-precipitated by the addition of 50% aqueous solution of 3.5 mol NaOH and Na_2CO_3 (anhydrous 0.943 mol) in distilled water. The addition took about 4 h and was carried out carefully with vigorous stirring at room temperature or below 35 °C. During the addition, the pH of the solution was maintained between 9 and 10. The slurry was cooled to room temperature, filtered and washed with deionized water until the pH of the wash water was 7. After drying at 100 ^oC for 24 h, the solids were calcined at 723 K for 12 h to get CHT(Calcined hydrotalcite).[43]

Catalyst Characterization

IR spectra of the samples pressed in KBr pellets were obtained with a Perkin Elmer instrument at a resolution of 2 cm^{-1} between 4000 cm^{-1} and 350 cm^{-1}, and in each case, the samples were referenced against a blank KBr pellet. Powder X-ray diffraction (XRD) patterns were obtained by using Cu Kα radiation (λ= 1.540562). Samples were step-scanned from 1 to 40 in 0.045 steps, with a stepping time of 0.5 s. The textural characterization of CaO and 5-15% Al_2O_3 loaded CaO were determined by physisorption of nitrogen BET surface area measurements (Micromeritics ASAP). The pore size distribution was calculated from the adsorption curve by BJH method. Surface area measurement and pore size distributions analysis were done, after pretreating the sample under high vacuum at 300 °C for 4 h, by nitrogen adsorption on a Micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K. Basic site density was measured by temperature programmed desorption of CO_2, pre-adsorbed at room temperature in a Micromeritics -2920 TPR/TPD analyser. Samples were treated in N_2 at 120 ^oC for 1 h, cooled to 27 ^oC and then exposed to 10 % v/v CO_2/He stream for 1 h. Weakly adsorbed CO_2 was removed by purging the samples with He at room temperature. The temperature was then increased at the rate of 10 ^0C/min from 27 to 700 ^0C; the amount of CO_2 chemisorbed and its desorption profile were then measured.

A TCD detector was used to measure the ammonia desorption profile. The elemental composition of prepared catalyst and its textural property were obtained by Energy Dispersive X-ray Spectroscopy (EDXS) on a KEVEX X-ray spectrometer and scanning electron micrograph.

Experimental set up

All experiments were performed in a stainless Parr autoclave of capacity 100 cm^3 equipped with a four blade-pitched turbine impeller. The temperature could be maintained at ±1 °C of the desired value with the help of in-built PID controller. The instrument was also equipped with a speed regulator that could maintain the speed at ±5 rpm of the desired speed. Predetermined quantities of reactants and the catalyst were charged into the autoclave and the temperature was raised to the desired value. Once the temperature was attained, an initial sample was withdrawn. Further samples were taken at periodic intervals. It took 15 min to get the reaction temperature to reach 120 °C and until then the reaction volume was not agitated. A typical standard experiment contained 0.01 mol furfural and 0.02 mol acetophenone with 0.0127 g/cm^3 catalyst loading, 120 °C temperature, agitated at 1000 rpm in ethanol solvent. Acetophenone was taken in excess and the conversion was based on disappearance of limiting reactant furfural.

Method of analysis of reaction mixture

Clear liquid samples were withdrawn from the reaction mass periodically and analyzed by gas chromatography on a Chemito 8610 model, SE-30 stainless steel packed column. The injector and detector temperatures were programmed from 100 °C to 280 °C with a ramp rate of 10 °C /min. Nitrogen was used as the carrier gas at a flow of 0.5 cm^3/s. Quantitative results were obtained through calibration by using synthetic mixtures of reactants and products. The conversion was based on decrease in concentration of limiting reactant furfural. The reaction products were confirmed by GC-MS.

Results and discussion

Scheme 1 depicts Claisen-Schmidt condensation of furfural with acetophenone. Preliminary experiments showed that among all synthesized catalysts, 15% w/w Al_2O_3/CaO was the best in both virgin and reused forms and hence its full characterization is reported here (Table 1).

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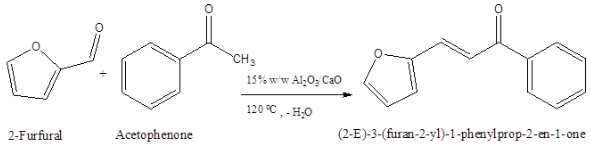

Scheme1:Claisen-Schmidt condensation of 2-furfural with acetophenone.

Table 1. Effect of Al_2O_3 loading on CaO: Activity of fresh and reused catalysts in reaction of furfural with acetophenone

Catalyst	Conversion,%			
	Fresh catalyst		Reused catalyst	
	1 h	2 h	1 h	2 h
CaO	58	88.5	30.3	55.6
5% w/wAl_2O_3/CaO	50	90.3	41.8	76.0
10% w/wAl_2O_3/CaO	65	100	59.1	92.1
15% w/wAl_2O_3/CaO	71.5	100	70.5	100

Reaction conditions: Furfural-0.01 mol, Acetophenone-0.02 mol, Catalyst loading 0.012 g/cm^3, Speed of agitation-1000 rpm, Temperature -120 °C, solvent-ethanol, Internal standard-n-Decane-200 µL

Catalyst characterization

FT-IR spectra of uncalcined and calcined 15% w/w Al_2O_3 on CaO are given in Figure 1 to determine the type of groups present in catalyst. In the case of uncalcined material, the sharp band at 3643 cm^{-1} is attributed to the stretching of hydrogen bonded to CaO and its bending mode at 712 cm^{-1}.[45]

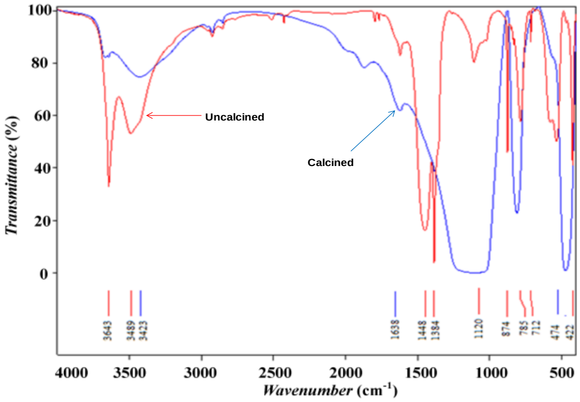

Fig. 1 FTIR of catalyst 15% w/w Al_2O_3/CaO

The weak band observed at 1120 cm^{-1} and strong band at 474 cm^{-1} is due to Al-O bond.[46] Asymmetric stretching of CO_3^{-2} is indicated by two bands at 1448 cm^{-1} and 1414 cm^{-1}. The weak band at 874 cm^{-1} is due to out of plane bending of CO_3^{-2}.[47,48] After calcination, the intensity of most of the bands is greatly reduced. The broad band at 3423 cm^{-1} is due to a sizeable amount of –OH groups which are still present at the surface. The small peak at 1638 cm^{-1} indicates water bending on the surface due to physically adsorbed water from atmosphere.[48]

XRD studies

The X-ray diffraction (XRD) patterns of uncalcined and calcined 15% w/w Al_2O_3/ CaO are shown in Figure 2. The strong diffraction peaks for CaO were seen in the catalyst calcined at 700 °C. The peaks for $Ca(OH)_2$ were also observed in the XRD profile of uncalcined sample. Calcination at 700 °C leads to decomposition of calcium hydroxide into calcium oxide. The calcined material shows major diffraction peaks at 32.2°, 37.4°, 53.9°, 63.2° and 67.5° which are characteristic peaks of CaO (JCPDS card No. 00-037-1497).

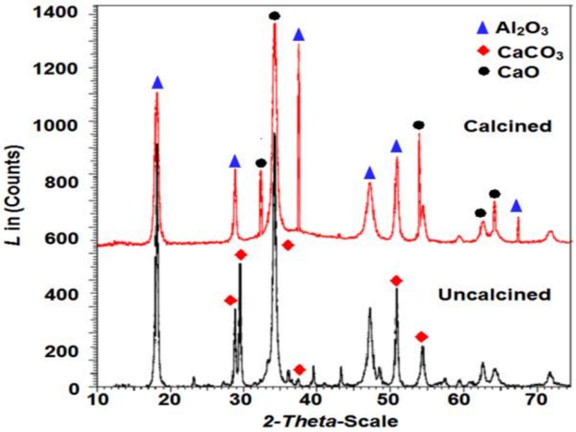

Fig. 2 XRD analysis of catalyst 15% w/w Al_2O_3/CaO

The results match with those of Matsuhashi et al.[50] The XRD patterns of both uncalcined and calcined catalysts show that there is not a single peak corresponding to $CaAl_2O_4$. Matsuhashi et al.[49,50] have reported that decomposition of an aluminium alkoxide on the surface of metal hydroxide in ethyl acetate is a better way to deposit alumina on metal oxides.[50] Figure 2 distinctly shows peaks for gibbsite phase of aluminium hydroxide. When the material was further calcined at 700 °C, the gibbsite phase was transformed into boehmite phase (JCPDS card no. 21-13070). In the case of 15% w/w Al_2O_3/MgO, high fraction of the Al^{+3} ions are in octahedral sites, probably due to substitution of Mg^{+2} ions by Al^{+3} ions.[49] Deposition of a layer of Al_2O_3 on the surface of CaO was expected as per literature.[49,50]

15% w/w Al_2O_3/CaO was very stable beyond 700 ° according to the TGA analysis (Figure 3). However, the loss in weight from 200 to 550 °C can be explained. A loss of about 3.9% weight was observed due to moisture present in the catalyst and also removal of CO_2 from the carbonate species used in the preparation. The weight loss below 200 °C was due to the loss of interlayer water and physically absorbed moisture. The next weight loss at 300 °C is attributed to hydroxyl group from the brucite-like layer of calcium hydroxide. Another loss close to 500 °C is because of CO_2 and CO_3^{-2} removal. The catalyst is very much stable above 550 °C.[49,50]

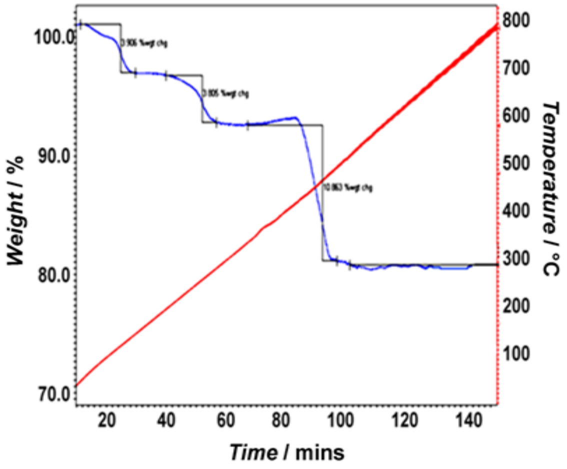

Fig. 3 TGA of 15% w/w Al_2O_3/CaO catalyst

BET surface area analysis

The catalyst shows characteristic type IV adsorption isotherms with well defined steps in nitrogen adsorption and desorption isotherms (Figure 4). There is a hysteresis in the adsorption-desorption isotherm at relative pressure (p/p_o) in the range of 0.4-0.94. The physical properties of CaO and 5 to 15% w/w Al_2O_3/CaO catalysts are shown in Table 1. There is a slight decrease in the surface area and pore volume of the CaO as the Al_2O_3 loading increases which suggest that aluminium oxide is being generated on the surface of CaO. The growth of crystalline Al_2O_3 on the CaO is also supported by XRD and FTIR. The average pore diameter 15% w/w Al_2O_3/CaO is found to be 11.0 nm. The explanation is in accordance with IUPAC classification.[52] The textural characteristics of catalyst with different loading of alumina on the calcium oxide are described in Table 2.

Table 2. Textural characteristics of catalyst with different loading of Al_2O_3 on CaO

Catalyst	S_{BET} $[m^2g^{-1}]^{[a]}$	D_{av} $[A°]^{[b]}$	V_{total} $[cm^3g^{-1}]^{[c]}$
CaO	55.61	92.6	0.15
5% w/w Al_2O_3/CaO	49.51	89.2	0.13
10% w/w Al_2O_3/CaO	43.96	90.0	0.12
15% w/w Al_2O_3/CaO	62.85	95.4	0.18

[a] BET surface area of various catalysts, [b] Average pore diameter (4 V/A)° by BET, [c] BJH pore volume.

CO_2- TPD analysis of 15% w/wAl_2O_3/CaO

CO_2-TPD was done for calcined 15% w/w Al_2O_3/CaO sample (Figure 5). There are basic sites of different strength consisting of low strength due to presence of hydroxyl groups and medium and strong basic sites due to basic oxygen atoms present on the surface of the catalyst. The two strong peaks at 394 °C and 665 °C correspond to 33.82 cm^3/g and 47.29 cm^3/g of CO_2 which was adsorbed at STP, respectively. These two peaks are responsible for generation superbasicity in the catalyst.

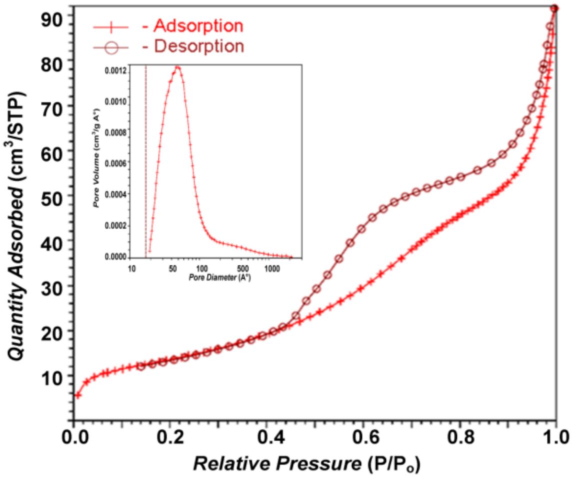

Fig. 4 N_2 adsorption ASAP of calcined catalyst 15% w/w Al_2O_3/CaO

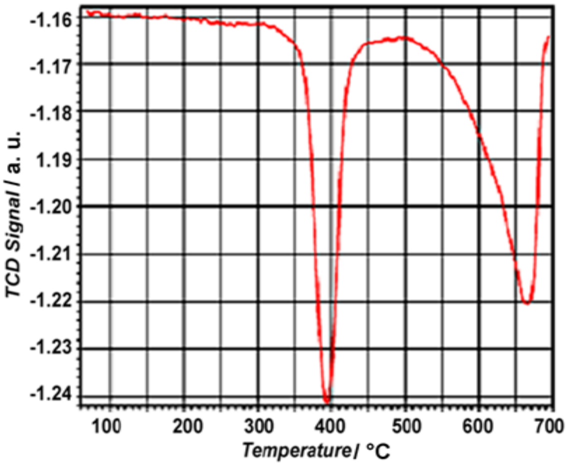

Fig. 5 CO_2- TPD of 15% w/wAl_2O_3/CaO

SEM of catalyst

The particle morphology SEM at various magnifications for uncalcined and calcined 15% w/w Al_2O_3 on CaO is shown in Figure 6. The SEM result also supports formation of large particle of $Ca(OH)_2$ with smooth planes and high degree of crystallinity, and incorporation of aluminium hydroxide on the surface of calcium hydroxide in uncalcined sample (Figure 6A and B). After calcination at 700 °C very rough surface was revealed (Figure 6C and D). The particle size was in the range of 1-5 µm.

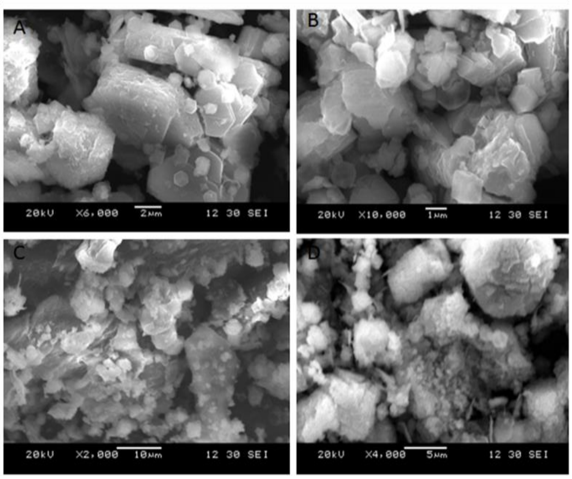

Fig. 6 SEM of uncalcined (A, B) and calcined catalysts (C, D)

Aluminium hydroxide was present on the surface as hexagonal plates like particles before calcination, whereas after calcination the structure was disturbed with an irregular morphology (Figure 6). Figure 7 gives EDXS analysis of 15% w/w Al_2O_3/CaO after calcination at 700 °C which shows the incorporation of alumina on surface of CaO (Table 3).

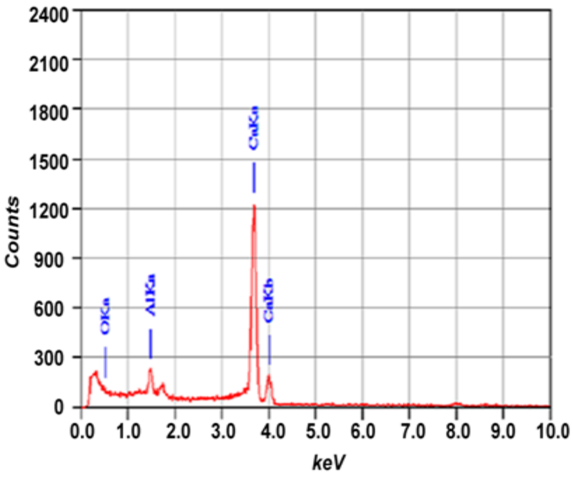

Fig. 7 EDXS analysis of 15% w/w Al_2O_3/CaO

Catalytic application

Claisen-Schmidt condensation of furfural with acetophenone for synthesis of 3-(furan-2-yl)-1-phenylprop-2-en-1-one was chosen to study the efficacy of a variety of catalysts (Scheme S1 in Supplementary Material). The effects of various catalysts on the yield of the product were studied.

Table 3. EXDS analysis

Element	Weight / %	Atomic / %
O	30.73	51.51
Ca	62.97	42.21
Al	6.30	6.28
Total	100	100

Catalyst Screening

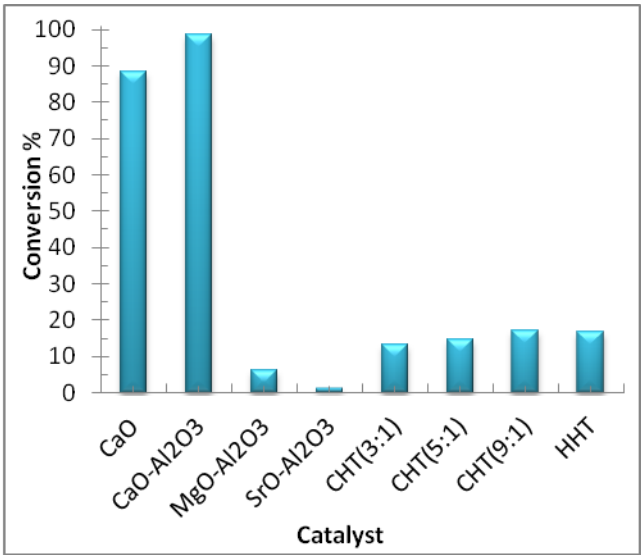

Fig. 8 Efficacy of various catalysts.

Reaction conditions: Furfural-0.01 mol, Acetophenone-0.02 mol, Catalyst loading- 0.012 g/cm^3, Speed of agitation-1000 rpm, Temperature -120 °C, solvent-ethanol, Internal standard-n-Decane-200 µL, Time – 2 h.

Various catalyst prepared by sol-gel method were screened under otherwise similar conditions. The activity of CaO, 15% w/w Al_2O_3 supported on CaO, MgO and SrO, hydrated hydrotalcite (HHT), calcined hydrotalcite (CHT) with different ratio of Mg:Al, are given in order to study the effect of mole ratio of Mg:Al on catalytic activity of CHT. For instance, CHT (3:1) stands for Mg:Al ratio in the CHT. Concentration profiles were monitored for each catalyst and the initial activity was calculated. The initial activity was the highest for 15% w/w Al_2O_3/CaO and it gave maximum conversion of 98.5% within 2 h for furfural to acetophenone mole ratio 1:2 at

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120 °C at a catalyst loading of 0.0127 g/cm^3 based on total volume of liquid (Figure 8). Pure calcium oxide obtained by calcination of $Ca(OH)_2$ at 700 °C gives 88.5% conversion in the same time but it has got very poor reusability. Therefore it was not selected for further study. Hattori et al.[53] have reported CaO and SrO as efficient catalysts for self condensation of furfural (called Tishchenko reaction to give 2-furylmethyl-2-furancarboxylate) at 80 °C. However, in the current work there was no self condensation over 15% w/w Al_2O_3/CaO. The activity of other alumina loaded catalyst was found to be very low (Figure 8). Uncalcined hydrotalcite with Mg: Al (3:1) gives 16.8% conversion whereas calcined hydrotalcite gives 13.4% conversion of the limiting reactant. We have also tested two calcined hydrotalcite (CHT) catalysts with mole ratio of Mg: Al as 5:1 and 9:1. Hardly 2% increase in the conversion was observed for CHT with Mg: Al ratio 9:1 as compared to Mg: Al ratio 5:1. Effect of loading of Al_2O_3 and reusability after 1 and 2 h reaction times is also given in Table 1 for all catalysts. The activity and reusability of 15% w/w Al_2O_3/CaO was found to be the best. These results are in agreement with Matsuhashi and co-workers.[49,50] Hence it can be concluded that loading of alumina on calcium oxide enhances its activity, stability and reusability of catalyst. Therefore 15% w/w Al_2O_3/CaO was selected for further investigation. Various parameters affecting rate of reaction and kinetic model of the reaction is given in supporting information.

Catalyst reusability

The reusability of 15% w/w Al_2O_3/CaO was tested by conducting 4 runs (Figure 9). After each run the catalyst was filtered and refluxed for 2 h with 50 cm^3 of ethanol in order to remove any adsorbed material from the pores. It was filtered and dried in an oven at 120 ºC for 2 h. Since there are losses of particles during filtration due to attrition, the actual quantity of catalyst used in next batch was almost 4-5% less than the previous batch. The volume of reaction mixture was adjusted to make up the catalyst loading of 0.0127 g/cm^3. It was observed that there is only marginal decrease in the conversion. Thus, the catalyst was active and reusable (Table 1).

Conclusions

15 % w/w Al_2O_3/CaO was synthesized and fully characterized by FT-IR, XRD, surface area analysis, TGA, SEM, EDXS, and CO_2-TPD. The catalyst possesses excellent activity and 100% selectivity for the Claisen-Schmidt condensation of furfuraldehyde with acetophenone. It gives the best result at a catalyst loading of 0.0127 g/cm^3, furfural to acetophenone mole ratio of 1:2, speed of agitation 1000 rpm and temperature of 120 °C. Since no side reaction such as aldol condensation or Tishchenko reaction was observed and the only coproduct is water, our methodology fits into the principles of green chemistry toward development of atom economical and sustainable synthesis of essential molecules. A detailed kinetics of reaction was also studied to establish that reaction obeys the Langmuir- Hinshelwood- Hougen-Watson (LHHW) mechanism with a very weak adsorption of reactants and follows the second order kinetics. The apparent energy of activation was found to be 12.5 kcal/mol (given as Supplementary Information).

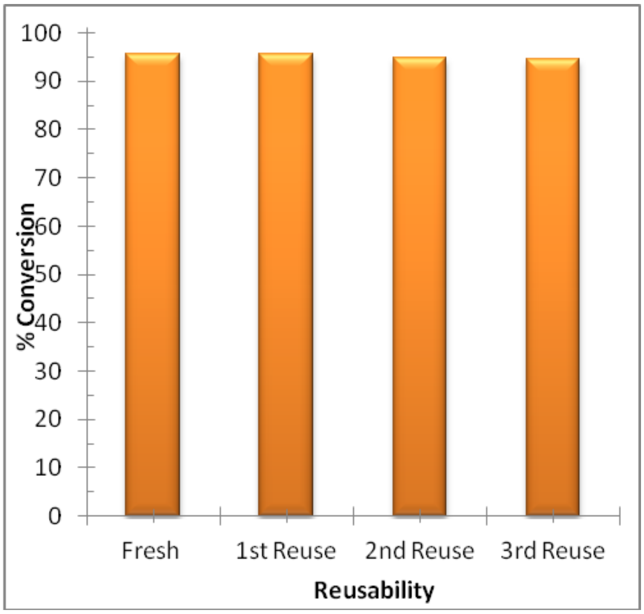

Fig. 9 Efficacy of reusability of catalyst
Reaction conditions: Catalyst-15%w/w Al_2O_3/CaO, Furfural-0.01 mol, Acetophenone-0.02 mol, Catalyst loading 0.012 g/cm^3, Speed of agitation-1000 rpm, Temperature -120 °C, solvent-ethanol, Internal standard-n-Decane-200 µL. Time- 2 h

In conclusion we have developed a simple, efficient, and environmentally benign method for the liquid phase Claisen-Schmidt condensation of furfural with acetophenone to produce 3-(furan-2-yl)-1-phenylprop-2-en-1-one.

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Notes and references

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Table of Contents Entry

Novelty of Claisen-Schmidt condensation of biomass-derived furfural with acetophenone over solid super base catalyst

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15% w/w Al_2O_3/CaO is an excellent and reusable catalyst for 100% selective condensation furfural with acetophenone to produce 3-(furan-2-yl)-1-phenylprop-2-en-1-one.