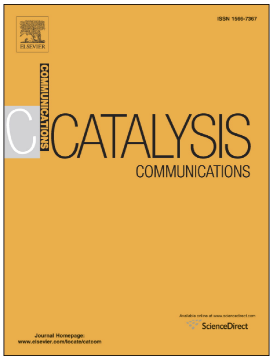

Pyridine immobilised on magnetic silica as an efficient solid base catalyst for Knoevenagel condensation of furfural with acetyl acetone

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PII: S1566-7367(19)30072-X
DOI: https://doi.org/10.1016/j.catcom.2019.03.005
Reference: CATCOM 5643

To appear in: *Catalysis Communications*

Received date: 14 January 2019
Revised date: 20 February 2019
Accepted date: 5 March 2019

Please cite this article as: K. Tarade, S. Shinde, S. Sakate, et al., Pyridine immobilised on magnetic silica as an efficient solid base catalyst for Knoevenagel condensation of furfural with acetyl acetone, Catalysis Communications, https://doi.org/10.1016/j.catcom.2019.03.005

Pyridine Immobilised on Magnetic Silica as an Efficient Solid Base Catalyst for Knoevenagel Condensation of Furfural with Acetyl acetone

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Abstract

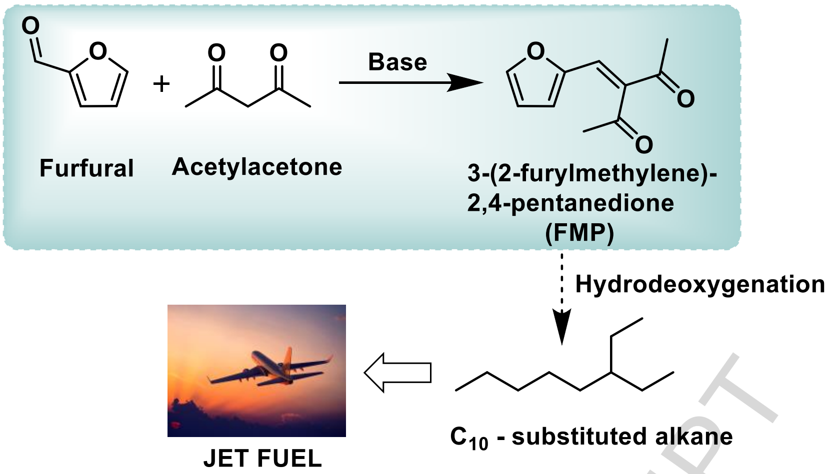
Novel heterogeneous pyridine immobilized magnetic silica ($Fe_3O_4@SiO_2$-Py) was found to be an efficient, greener and heterogeneous solid base catalyst for the Knoevenagel condensation of furfural with acetylacetone under optimized reaction conditions. The Knoevenagel condensation product 3-(2-furylmethylene)-2,4-pentanedione (FMP), a jet fuel precursor, was produced in high yield of 85 % with 94 % conversion of furfural at 100 ^{o}C within a period of 4 h. $Fe_3O_4@SiO_2$-Py catalyst showed excellent stability and recyclability without losing its initial activity.

Key words: Knoevenagel condensation, furfural, silica immobilised pyridine, solid base, jet fuel.

1. Introduction

Currently chemicals and liquid fuels are largely produced from crude oil however, the sources of crude oil will be on the verge of diminishing in near future. In addition, during crude oil refining process, huge amount of CO_2 is expelled out causing irreparable air pollution. Fortunately, these threats can be overcome by utilising lignocellulosic biomass which is as a sustainable carbon source and green alternative to crude oil [1]. Furfural is the most important platform molecule produced by the hydrolysis and dehydration of xylan contained in lignocellulosic biomass. Diesel-range long chain alkanes can be produced from furfural via acid or base catalyzed C−C bond formation followed by hydrodeoxygenation [2, 3]. In this context, aldol, Knoevenagel condensations [4, 5], Baylis−Hillman, coupling reactions [6, 7], and HAA reaction [8-10] can be performed for carbon upgradation of furfural. These upgraded products are carbon-rich and can be converted into liquid hydrocarbons *via* ring-opening−dehydration−hydrodeoxygenation processes [11, 12]. In particular, the Knoevenagel condensation of furfural is not studied much. For instance, Ding et al. demonstrated enzyme (lipoprotein lipase) catalyzed Knoevenagel condensation between furfural and acetyl acetone at 35 °C. However, this catalytic system required long reaction time of 48 h and gave moderate yield (76 %) in dimethyl sulfoxide solvent [13]. Very recently, Appaturi et al. developed alanine functionalized MCM-41 catalyst for Knoevenagel condensation between furfural with acetyl acetone. Under the solvent-free condition and in a short reaction time (30 min) this catalyst system provided 100% selectivity to α,β-unsaturated products with 92% conversion of furfural [5]. Several organic–inorganic hybrid materials containing N-containing organic functionalities such as pyridine-functionalized porous polymers [14], DABCO based ionic liquid [15], primary amine functionalized MCM-41 [16, 17] and organic polymer [18] have been found successful for the Knoevenagel condensation of active methylene compounds with aldehydes.

With this background in this study, we report a magnetically separable silica immobilised pyridine ($Fe_3O_4@SiO_2$-Py) (Scheme 2) as an effective solid base catalyst that shows excellent performance for the Knoevenagel condensation of furfural with acetyl acetone (Scheme 1). $Fe_3O_4@SiO_2$-Py catalyst showed the highest conversion of furfural (94 %) with 85 % yield of condensation product at 100 ^{o}C in the absence of solvent. This novel catalyst showed reusability up to six times without significant decrease in activity and selectivity.



Scheme 1. Synthesis of Jet fuel precursors from furfural and acetyl acetone

2. Experimental

2.1. Materials

Furfural, N,N-dimethylaminopyridine, furfurylamine, DBU, 4-hydroxypyridine, 3-pyridinecarbaldehyde 3-aminopropyltriethoxysilane, tetraethyl orthosilicate, $FeCl_2$ and $FeCl_3$ were purchased from Sigma-Aldrich. Sodium hydroxide, triethylamine, zinc oxide, calcium oxide and aq. ammonia (10%) were obtained from Thomas-Baker. Acetylacetone was purchased from Merk, India. Methanol, toluene, pyridine, dichloromethane, ethyl acetate and petroleum ether and silica gel (230-400 mesh) were purchased from Chem Labs, India.

2.2. Preparation of 3-aminopropylsilica

To a solution of 3-aminopropyltriethoxysilane (3.5 g) in toluene, pyridine (1:1, 20 mL), SiO_2 (2 g, 230-400 mesh) were added. The resulting mixture was refluxed for 24 h under N_2 atmosphere after which the reaction mixture was filtered and residue was washed with toluene (20 mL x 1) and dichloromethane (20 mL x 1). The residue was dried in oven for 24 h to afford off a white powder (4.8 g).

2.3. Preparation of silica-pyridine (SiO_2-Py)

Step 1(1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methanimine): A mixture of 1.8 g of 3-aminopropyltriethoxysilane (AMPSi), 3-pyridinecarbaldehyde (0.877 g) and dichloromethane (25 mL) was stirred at 50 ^{o}C for 24 h and then the solvent was evaporated on rotary evaporator to afford a colorless oil (2.5 g).

Step 2 (1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methanimine-silica): To a solution of 1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methanimine (2.5 g) in toluene (20 mL), SiO_2 (1.7 g, 230-400 mesh) was added. The resulting mixture was refluxed for 24 h under N_2 atmosphere and then filtered to give a residue which was washed with toluene (20 mL x 1) and dichloromethane (20 mL x 1). The residue was dried in oven for 24 h to afford off white powder (4.0 g).

Step 3 (N-(pyridin-3-ylmethyl)propylamino-silica)[19]: A mixture of 1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methaniminesilica (3.5 g) and methanol (25 mL) was cooled at 0 ^{o}C and $NaBH_4$ (0.619 g) was added. The resultant mixture was stirred at room temperature for 24 h then evaporated to afford off white powder (3.2 g).

2.4. Synthesis of nano-magnetite particles (Fe_3O_4)

A solution of $FeCl_2$ (5.4 g) and $FeCl_3$ (2 g) in aqueous hydrochloride acid (2 M, 25 mL) were sonicated at room temperature until the salts dissolved completely. To this solution, an aqueous ammonia solution (25%, 40 mL) was added slowly under argon atmosphere followed by 30 minute stirring. The Fe_3O_4 nanoparticles were separated by external magnet and washed with deionized water (3 x 50 mL) and ethanol (3 x 50 mL) and dried under vacuum (Scheme 2).

2.5. Synthesis of silica-coated magnetite nanoparticles (SMNP)

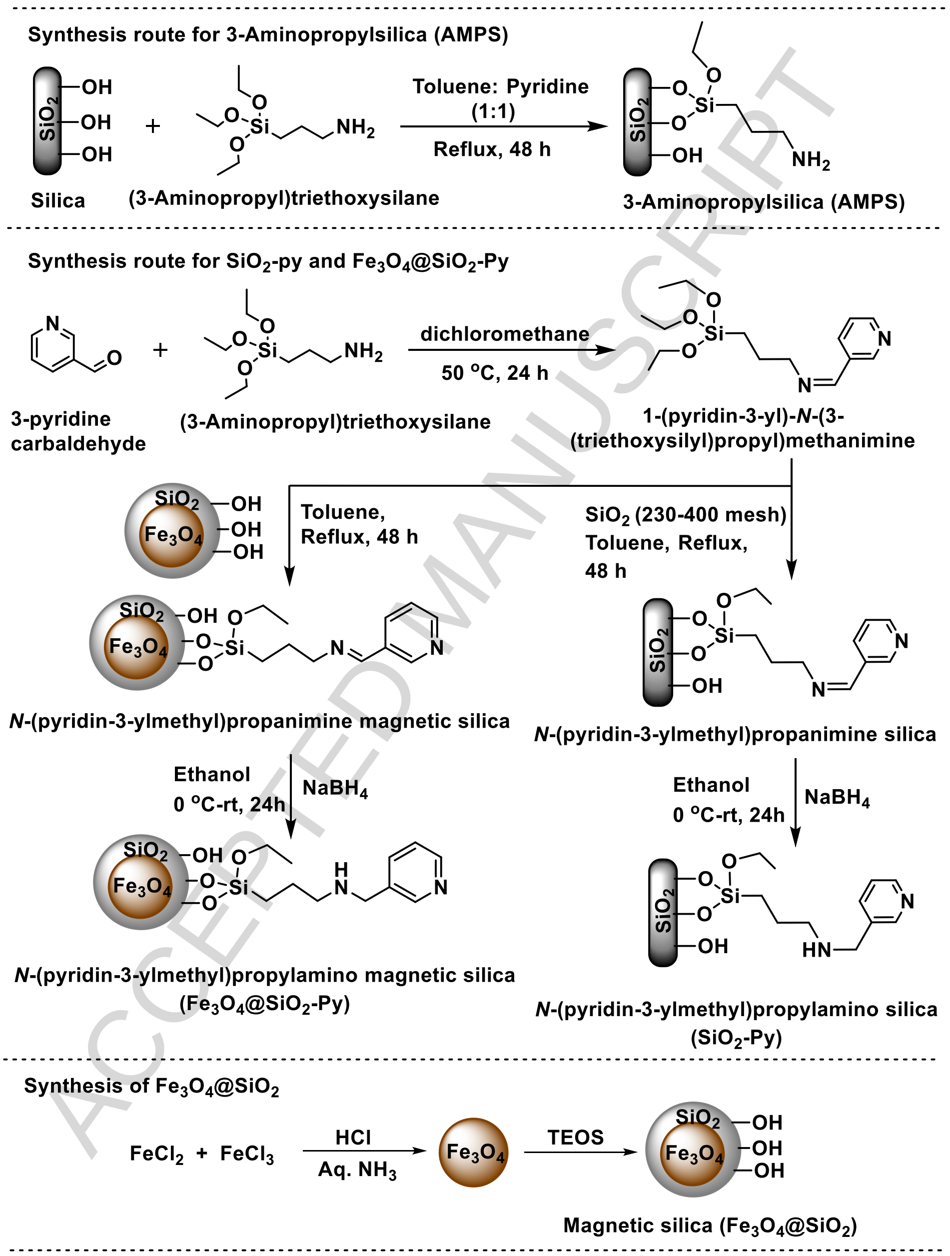
The synthesized Fe_3O_4 suspended in 35 mL ethanol and 6 mL deionized water and sonicated for 15 min then 1.5 mL of tetraethyl orthosilicate (TEOS) was added slowly and again sonicated for 10 min. Then aqueous ammonia (10%, 1.4 mL) was added slowly under stirrer and mixture was heated at 40 ^oC for 12 h. The iron oxide nanoparticles with a thin layer of silica ($Fe_3O_4@SiO_2$) were separated by an external magnet and washed three times with ethanol and dried under vacuum.

2.6. Preparation of $Fe_3O_4@SiO_2$-Py

To a solution of 1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methanimine (2.5 g) in toluene (20 mL), $Fe_3O_4@SiO_2$ (10 g) was added lot-wise. The resulting mixture was refluxed for 24 h under N_2 atmosphere. Reaction mixture was filtered; residue was washed with toluene (20 mL x 1) and dichloromethane (20 mL x 1). Then the residue was dried in oven for 24 h to afford off white powder (4.0 g) of 1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methanimine magnetic silica. Further a mixture of 1-(pyridin-3-yl)-N-(3-(triethoxysilyl)propyl)methanimine magnetic silica (4.0 g) and methanol (25 mL) was cooled at 0 ^oC and $NaBH_4$ (0.69 g) was added. The resultant mixture was stirred at room temperature for 24 h then evaporated to afford off white powder (3.6 g) of $Fe_3O_4@SiO_2$-Py (surface are of 138 m^2/g).

2.7. Catalyst Test

A mixture of furfural (0.192 g, 2 mmol), acetylacetone (0.2 g, 2 mmol) and $Fe_3O_4@SiO_2$-Py (0.1 g) was stirred at 100 ^oC for 4 h after which the catalyst was separated by an external magnet and the resultant reaction mixture was diluted with ethyl acetate (20 mL x 1) and subsequently washed with water (20 mL x 1) and brine solution (20 mL x 1). Then reaction mixture was dried over sodium sulfate and evaporated under reduced pressure. The obtained crude oil was purified by column chromatography using ethyl acetate: petroleum ether (2: 98; *v*/*v*) eluent to afford yellowish brown liquid. After reaction catalyst was hold with external magnet and reaction mass was decanted and the catalyst was subsequently washed with ethyl acetate and reused for next run.



Scheme 2. Synthesis routes for 3-Aminopropylsilica, Fe_3O_4@SiO_2-Py and SiO_2-Py and Fe_3O_4@SiO_2

3. Results and discussion

3.1. Catalyst characterisation

3.1.1. FTIR

Structures of organosilica catalysts were confirmed by FTIR analysis (Figure 1). In the $Fe_3O_4@SiO_2$-Py catalyst, intense peaks between 580 cm^{-1} and 630 cm^{-1} were attributed to the stretching vibration mode associated with metal-oxygen (Fe-O) bonds in the crystalline lattice of Fe_3O_4. A band at 1647 cm^{-1} was attributed to –C=N- of pyridine moiety and band at 3375 cm^{-1} was for hydroxyl functionality. FTIR pattern of $Fe_3O_4@SiO_2$-Py and SiO_2-Py was almost similar except that Fe_3O_4 pattern. Aminopropylsilica showed bands at 1020 cm^{-1} and 1472 cm^{-1} for Si-O-Si and –NH_2 functionality, respectively.

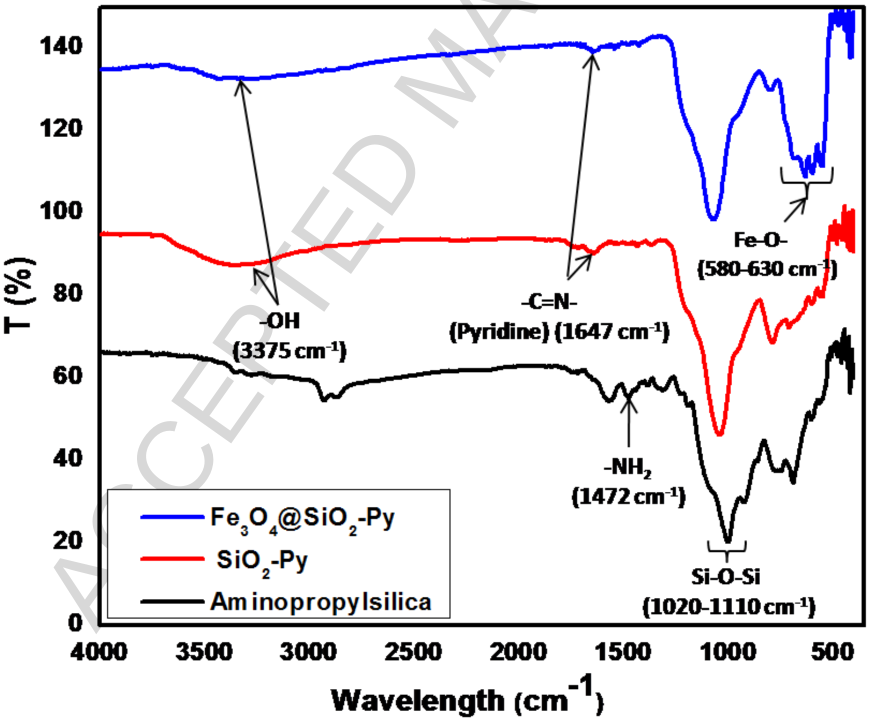


Figure 1. FTIR of 3-Aminopropylsilica, Py-SiO_2 and $Fe_3O_4@SiO_2$-Py catalysts

3.1.2. Solid state NMR

The structure of SiO_2-Py catalyst was confirmed by solid state ^{13}C NMR (Figure S3) in which, three well resolved lines at 50.38, 22.23, and 10.53 ppm were observed and assigned to –CH_2- groups as d, c, b and a, respectively. The bands at 125, 136.13, 138.24 and 148.56 ppm are assigned to –CH- groups of pyridine with carbon atoms numbered e, f, g and h, respectively.

3.1.3. XRD

To confirm the presence of Fe_3O_4 phases, XRD pattern of Fe_3O_4@SiO_2-Py was compared with the standard Fe_3O_4 (Figure S2). A series of characteristic peaks such as (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) were observed in the Fe_3O_4@SiO_2-Py sample which are in well accordance with the inverse cubic spinel phase of Fe_3O_4 (JCPDS 85-1436).

3.1.3. TEM

Morphology and particles size of Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-Py and Fe_3O_4@SiO_2-Py(reused) samples was investigated by using TEM analysis (Figure S1). The results indicate that Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-Py and Fe_3O_4@SiO_2-Py(reused) have almost a hexagonal shape with an average particle size of 36, 40 and 41 nm, respectively. Figure S1 clearly showed that nanoclusters of Fe_3O_4 were successfully coated with a thin layer of SiO_2 leading to core/shell structure of Fe_3O_4@SiO_2 NPs. Morphology and particle size of Fe_3O_4@SiO_2-Py sample has been retained even after its reuse which proves stability of the catalyst (Figure S1).

3.1.2. Catalyst screening for Knoevenagel condensation of furfural with acetylacetone

The Knoevenagel condensation reaction is usually facilitated by using basic catalysts. In this work, several basic catalysts were tested for the Knoevenagel condensation of furfural with acetylacetone (Table 1). Initially, furfural was treated with acetylacetone in presence of NaOH at 80 ^oC for 4 h to give the Knoevenagel product (FMP) in 78 % yield with 95 %

conversion of furfural (Table 1, entry 1). Indeed, use of homogeneous base catalyst is unattractive due to downsides such as non-reusable, hazardous waste generation and it also need to be neutralized with acids which ultimately increases the process operations. Therefore, easily recoverable and environmentally compatible solid bases are usually most preferred. In this direction, we performed Knoevenagel condensation over series of solid bases. For instance, with hydrotalcite (Mg/Al = 3) at 100 ºC, FMP was formed in 31 % yield with only 56 % conversion of furfural (Table 1, entry 2). In presence of CaO, FMP was produced in 41 % yield with 67 % conversion of furfural (Table 1, entry 3). With ZnO-400 catalyst, FMP obtained was in 29 % yield with lower conversion (41%) of furfural (Table 1, entry 4). Although, the basic metal oxides gave 100 % selectivity for FMP but the yield was low to moderate due to lower conversion of furfural. Generally, the Knoevenagel condensation is more prone over amine containing organic bases. In presence of catalytic amount of triethylamine, 79 % yield of FMP was achieved with 89 % conversion of furfural (Table 1, entry 5). Biomass derived furfurylamine as a catalyst showed similar activity as of triethylamine (Table 1, entry 6). Further, with N,N-dimethylaminopyridine (DMAP) the FMP was obtained in 77 % yield (Table 1, entry 7). In presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) catalyst, the FMP was formed in 78 % yield (Table 1, entry 8). With 4-hydroxypyridine, furfural was consumed upto 95 % and 83 % yield of FMP was achieved (Table 1, entry 9). Amine functionalized homogeneous bases gave good yield and 99 % selectivity to the FMP with almost 90 % conversion of furfural. Homogeneous bases are not only non-recyclable but they are soluble in organic solvent hence, they could contaminate the product. However, these catalysts can be heterogenized by anchoring amine functionalized organic amines on silica. For instance, 3-Aminopropylsilica was used for this reaction however a moderate yield (76 %) of FMP with 99 % selectivity was noticed with almost 90 % conversion of furfural (Table 1, entry 10). Pyridine anchored on silica (SiO_2-Py) showed better catalytic performance than 3-Aminopropylsilica. With SiO_2-Py catalyst, a 94% conversion of furfural was achieved to obtain 85% yield of FMP (Table 1, entry 11). In case of SiO_2-Py catalyst, pyridine moiety is planar and the lone pair of electrons are present perpendicular to the plane of pyridine. Hence, hydrogen from the active methylene group of acetylacetone can be easily approached. On the contrary, in 3-Aminopropylsilica, catalyst amine functionality is distorted tetrahedral structure which creates some hinderance for the reactant as compared to pyridine. Due to these reasons SiO_2-Py showed better activity than 3-Aminopropylsilica. $Fe_3O_4@SiO_2$-Py catalyst showed similar activity to that of SiO_2-Py (Table 1, entry 12). Use of magnetic catalyst ($Fe_3O_4@SiO_2$-Py) is advantageous over SiO_2-Py because, the former can be easily separated with help of external magnate. While, in case of SiO_2-Py catalyst recovery is done by filtration which is associated with handling losses.

Table 1. Catalyst screening for Knoevenagel condensation of furfural with acetylacetone [a]

Entry	Catalyst	Loading	T [°C]	Conv.[b] [%]	Yield[b] [%]	Sel.[b] [%]
1	NaOH	10 mol%	80	95	78	92
2	Hydrotalcite	0.1 g	100	56	31	100
3	CaO	0.1 g	100	67	41	100
4	ZnO-400	0.1 g	100	41	29	100
5	Triethylamine	10 mol%	100	89	79	99
6	Furfurylamine	10 mol%	100	90	80	99
7	DMAP	10 mol%	100	85	77	98
8	DBU	10 mol%	100	87	78	99
9	4-Hydroxypyridine	10 mol%	100	95	83	99
10	3-Aminopropylsilica	0.1 g	100	81	76	99
11	SiO_2-Py	0.1 g	100	94	85	100
12	$Fe_3O_4@SiO_2$-Py	0.1 g	100	94	85	100

[a] Reaction condition: Furfural (0.196 g, 2 mmol), catalyst, acetylacetone (0.2 g, 2 mmol), 4 h. [b] Yields are determined using HPLC.

3.1.3. Effect of temperature

The yield of FMP was increased gradually with rise in temperature from 80-100 °C and reached maximum (85%) at 100 °C. Further increase in temperature to 110 °C, the yield of FMP not improved (Figure 2).

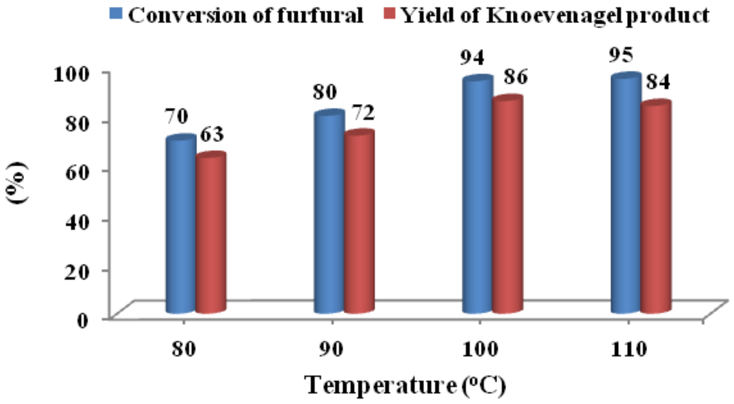


Figure 2. Influence of temperature. Reaction conditions: Furfural (0.192 g, 2 mmol), acetyl acetone (0.2 g, 2 mmol), $Fe_3O_4@SiO_2$-Py (0.1 g), 4 h.

3.1.4. Effect of time

Up to 85% furfural conversion with 78% yield of FMP was observed within just 1.5 h. After that conversion of furfural and yield of FMP was slowly increased. At the end of 4th hour maximum conversion of furfural and yield of FMP was achieved. Extending reaction beyond 4 h did not show any improvement in reaction progress (Figure 3).

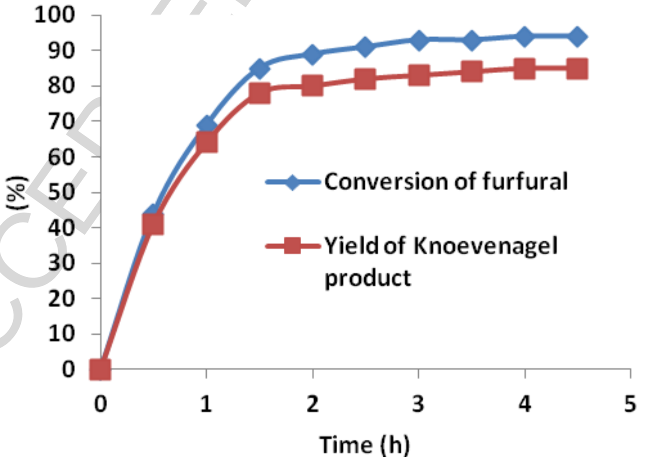


Figure 3. Influence of time. Reaction conditions: Furfural (0.192 g, 2 mmol), acetylacetone (0.2 g, 2 mmol), $Fe_3O_4@SiO_2$-Py (0.1 g), 0-5 h.

3.1.5. Effect of catalyst amount

Influence of catalyst amount in the range of 0.05-0.150 g was investigated for this reaction (Figure 4). With 0.05 g of Fe_3O_4@SiO_2-Py the yield of FMP was only 61% and while, increasing the amount to 0.075 g resulted in enhancement of the yield of FMP (79%). The lower catalyst amount gave lower yield due to insufficient active site. However, with catalyst amount 0.15 g the yield of FMP was comparable with that of 0.1 g.

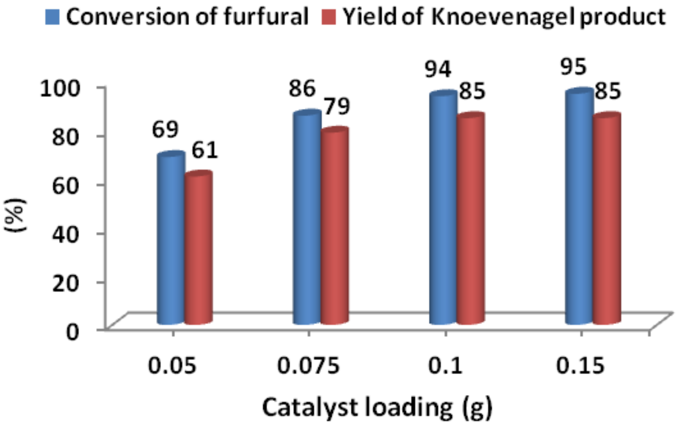


Figure 4. Influence of catalyst amount. Reaction conditions: Furfural (0.192 g, 2 mmol), acetylacetone (0.2 g, 2 mmol), Fe_3O_4@SiO_2-Py (0.05 - 0.15 g), 4 h.

3.1.6. Recycle study

The stability of Fe_3O_4@SiO_2-Py was evaluated by performing recycle runs (Figure S6). It was found that the catalytic activity of Fe_3O_4@SiO_2-Py was very much consistent after being used for six times.

4. Conclusions

We presented here a simple and robust Fe_3O_4@SiO_2-Py catalyst system for the Knoevenagel condensation of furfural with acetyl acetone to achieve high yield of FMP. The condensation product FMP is a unit of C_{10} and could be converted into branched alkanes (Jet fuel) through hydrodeoxygenation process. The stability of the Fe_3O_4@SiO_2-Py is confirmed by its several reuses.

Acknowledgements

S.H.S is grateful to CSIR-National Chemical Laboratory, AcSIR and CSIR.

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Highlights

- Solid base catalyst prepared by anchoring pyridine on magnetic silica
- Fe_3O_4@SiO_2-Py catalyzed Knoevenagel condensation of furfural with acetyl acetone
- Structural characterization of Fe_3O_4@SiO_2-Py confirmed by NMR and FTIR
- The catalyst successfully recycled for six consecutive runs