



Potassium Fluoride/ K10-montmorillonite Nanostructure as a Green and Reusable Catalyst Under mild Reaction Conditions for the Knoevenagel Condensation

MERCEDEH GHANEI¹,
MOHAMMAD A. KHALILZADEH^{2,*} and MOHAMMAD M. HASHEMI¹

¹Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.

²Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran.

*Corresponding author E-mail: m.khalilzadeh@hotmail.com

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ABSTRACT

Potassium fluoride (KF)/montmorillonite (K10-MMT) nanostructure acts as an active heterogeneous base catalyst for Knoevenagel condensation. Here we have described the catalytic activities of KF/K10 nanostructure in the condensation reaction of various substituted benzaldehydes with active methylene compound malononitrile under mild condition. The experimental results showed that the KF/K10 had high catalytic activity and it can be recycled without significant loss of activity. This practical and eco-friendly protocol provides a facile way to C-C bond formation under mild conditions.

Key words: Potassium fluoride, Montmorillonite, Carbon-Carbon bond, Solid base catalyst, Knoevenagel condensation.

INTRODUCTION

Formation of C-C bonds is one of the significant objectives in organic synthesis, particularly in the synthesis of fine chemical products. Knoevenagel condensation is one of the well documented reactions for forming electrophilic olefins and C-C bond between carbonyl compounds and active methylene compounds. This reaction is a practical method to achieve fine chemical

intermediates and therapeutic and pharmacological products¹⁻³.

Owing to their importance from an industrial, pharmacological and synthetic point of view a great number of methods for the Knoevenagel condensation have been developed using various Lewis acids/bases under ultrasound and microwave irradiation, using green solvent like water or ionic liquid, and grindstone method under solvent-free condition⁴⁻¹². However, most of the reported reagents

suffer from disadvantages such as high cost reagent, tedious work-up, environmental limitations, disposal problems and so on. In order to cumbersome these problems, emphasis has been laid on the use of supported reagents. The major advantage of supported reagent is the reusability of the catalyst that makes the process inexpensive. Furthermore, it also contributes towards the area of "Green Chemistry"¹³.

Solid base is a vital variety of catalysts offering excellent opportunities for replacing of reducing operating costs associated with base neutralization and product purification, diminishing corrosion and other related environmental problems, and in the meantime allowing easier separation and reusable of the catalysts. Moreover, solid bases also have the advantages of nontoxicity, eco-friendliness and easy work-up procedure¹⁴⁻¹⁶.

Among the salts with potentially basic properties potassium fluoride (KF) is more general owing to its cheapness and availability. A lot of supports have been introduced for increasing the basicity of KF such as KF/ZnO, KF/Ca-Mg-Al, KF/CaO-Fe₃O₄, KF/celite, KF/zeolite, and KF/LDH mainly applied for organic production. Although, a majority of the abovementioned solid bases are effective in organic transformations, they suffer from some drawbacks such as low basicity, use of expensive solid supports and tedious preparation steps¹⁷⁻²⁵.

Montmorillonite (MMT) clay having two silica tetrahedral sheets layered between one alumina octahedral sheets. MMT is a clay mineral with a large specific exhibits good adsorbability, surface area, cation exchange capacity. K10-MMT is known

to behave as heterogeneous catalysis in organic reactions. Consequently, we thought to employ a new type of solid acid-base catalyst, where the base is electrostatic bond onto a solid acidic support towards the desired reaction²⁶⁻²⁸.

K10-MMT has high cation exchange capacity specifically, so use of this property by impregnation of potassium fluoride on MMT reasons a more free fluoride anion, which is able to act as an effective base²⁹.

With attention to above details, this research indicated that K10/KF nanostructure can be used as an suitable heterogeneous basic catalyst for solvent-free methods based on green chemistry to improve the Knoevenagel condensation reaction by condensation of phenolic compounds with methyl acetoacetate. Finally In the context of our work this catalyst is desirable alternative, owing to its non-toxicity, low-cost and eco-friendly properties.

MATERIALS AND METHODS

All starting materials and chemical solvents were purchased from Aldrich and Merck were used without further purification.

Preparation of the Catalyst

The catalyst was prepared according to the literature procedure; prepared by dissolving KF (5.5 g) in distilled water (10 mL) and K10-MMT (10 g). The mixture was stirred for 1 h next, the water was removed at 60–70 °C in a rotary evaporator under reduced pressure. The resulted solid mixture was further dried at 70–80 °C in a vacuum drying oven for 30 h.

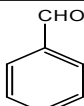
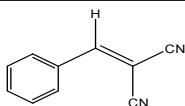
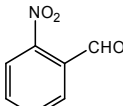
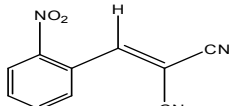
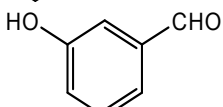
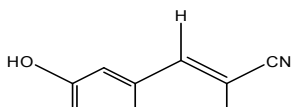
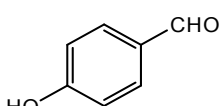
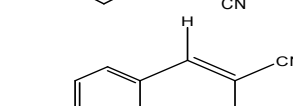
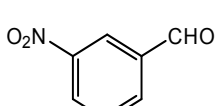
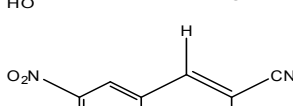
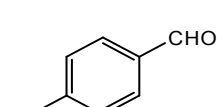
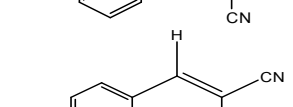
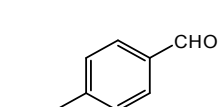
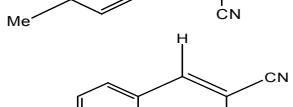
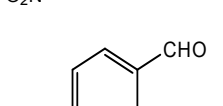
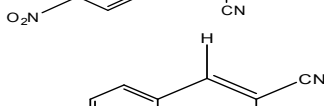
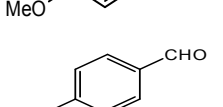
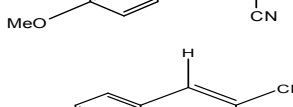
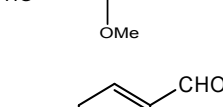
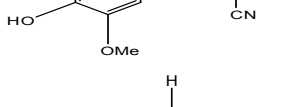
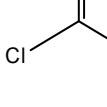
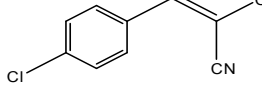
Typical procedure for the Knoevenagel condensation

In a typical reaction, substituted aromatic aldehyde (1 mmol), malononitrile (1.01 mmol), and 0.1 g of catalyst (KF/K10) were placed in a glass flask equipped with a magnetic stirrer at 100 °C for 10-25 min. Then, the reaction was allowed to cool to room temperature after completion of the reaction (monitored by TLC). Then a solid precipitate was separated out, filtered and washed with water (3 x 10 mL) followed by ethanol (3 x 10 mL), and dried under vacuum. In this case approximate temperature

Table 1: The effect of different solvents on the course of reaction

Yield %	Time (min)	Solvent	
45	80	Acetonitrile	1
60	90	Water	2
94	10	Ethanol	3
35	180	Chloroform	4
80	30	Solvent-free	5

Table 2: Knoevenagel reaction catalyzed by KF/K10

Entry	Aldehydes	Time (min)	Product	Melting point (°C)	Yield ^[a] (%)
1		10		80-82 °C	94
2		10		135-137 °C	95
3		20		162-165 °C	90
4		20		185-188 °C	89
5		15		107-109 °C	91
6		20		133-135 °C	95
7		25		159-162 °C	93
8		25		114-116 °C	88
9		30		134-136 °C	94
10		20		163-164	95
11		20		48-51	94

12		20		131-134	91
13		15		124-127	90
14		20		78-81	87
15		25		93-95	93

was obtained by using sealed capillaries containing compounds of known melting point within the reaction container.

RESULTS AND DISCUSSION

Catalytic applications of KF/K10 for Knoevenagel condensation

The catalytic activity of KF/K10 nanostructure was used as an appropriate heterogeneous basic catalyst for solvent-free protocol Knoevenagel condensation by condensation of benzaldehyde with malononitrile.

To optimize the reaction conditions, benzaldehyde and malononitrile were selected as the model substrates to examine the effects of different solvents and molar ratios of the catalyst at different temperatures. The effect of different solvents on the course of reaction was studied (Table 1). From the results given in Table 1, it was found that among various solvents tried, ethanol was found to give optimum results in terms of reaction time and yield. Consequently, the optimum conditions for the

reaction are: benzaldehyde (1 mmol), malononitrile (1.01 mmol) and 0.16 g of KF/K10 nanostructure, 60 °C was found to be the optimum reaction temperature as at low temperature, reaction time was longer.

In order to generalize the scope of reaction, a variety of aldehydes was subjected for reaction with malononitrile under the mild optimized reaction conditions, and the results are presented in Table 2. The spectral data and melting points are in good agreement with those reported in literature. The

Table 3: Recycling of KF/K10 nanostructure in Knoevenagel reaction by condensation reaction of benzaldehyde and malononitrile

CYCLE	TIME (MIN)	YIELD (%)
1	12	94
2	12	92
3	15	90
4	20	86
5	20	83

reactions went on well to afford products in good to high yields and short times.

It was concluded that the reuse of a heterogeneous system and the lifetime of the catalyst are highly preferable in terms of green chemistry. This research used the recycled catalytic five times without any reduction in the chemical reaction. The efficiency of the catalytic activity after five times recycling reached to 83% down from 94% as illustrated in Table 3.

CONCLUSIONS

In this research, we supported KF on the MMT. The research found that KF/K10 is a proper nanocatalyst with a high stability for Knoevenagel condensation. The advantages of the present method are simplicity of work-up, high yields, short reaction times and recyclability of the catalyst.

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