



## An active and selective heterogeneous catalytic system for Michael addition

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### Abstract

Potassium fluoride doped natural zeolite was found to be an efficient and selective solid base catalyst for 1,4-Michael addition. The catalyst is easily prepared and the workup procedure simplified by simple filtration. All products were obtained in high yields as well as short reaction times.

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The current attention toward environmentally friendly, efficient syntheses and economic advantage of zeolites and zeotype-materials has driven the generation of new strategies for heterogeneous catalysts to facilitate product recovery, catalyst reuse, reaction workup, and waste disposal [1].

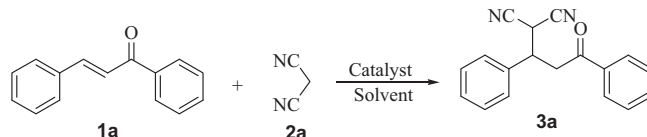
Impregnation of a catalyst to an appropriate solid matrix is a well-known approach to catalyst recovery and reuse [2]. Creation of C–C bond *via* Michael reaction is a highly utilized tool in organic transformations, and it is usually catalyzed by bases under homogeneous conditions [3].

There are many reports available under the category of heterogeneous catalysis for Michael additions mediated particularly by Ba(OH)<sub>2</sub> [4a], KF on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [4b], hydrotalcites [4c–e], organic resins [4f], MgLa mixed oxides [4g], magnesium oxide fluorides [4h], KG-60-NEt<sub>2</sub> [4i], [bmIm]OH [4j], KF on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [4k], KF doped phosphates [4l], surface-anchored amines [4m], high surface area MgO [4n], *N*-phenyl-tris(dimethylamino)iminophosphorane (P-BEMP) immobilized on polystyrene resin [4o], and silica gel 60 [4p], vanadium-apatite [4q], organic-inorganic hybrid catalysts [4r].

However there are some problems using mentioned systems such as the use of expensive or toxic materials and tedious or time-consuming reagent preparation. Thus, it is clear that there is considerable scope for development of more applicable heterogeneous catalysts for industrial applications.

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Scheme 1.

Clinoptilolite is an environmentally friendly, nontoxic and inexpensive natural zeolite which is commercially available. It can act as cation scavenger and this unique property made it possible to increase the basicity of some anions [5]. We recently demonstrated that a potassium fluoride impregnated on clinoptilolite is exceedingly strong base to be useful in SNAr and Ullmann reaction [6].

In this study, we describe an efficient solid base for 1,4-addition reactions. In our continued efforts for the development of the solid base catalysts for organic transformations, herein we report a fast and selective 1,4-addition reactions in the presence of a solid base catalyst (KF/CP) by direct condensation of various active methylene compounds and chalcones. The reaction conditions are optimized, to obtain exclusively the appropriate products in quantitative yields (Scheme 1).

To optimize the reaction conditions, a variety of soluble and solid base catalysts have been explored on chalcone, chosen as model reactants in the presence of malononitrile (Table 1).

The basicity results correlated with the CP tendency for cation absorption (Table 1, entries 4 and 5). Nearly, complete conversion toward the corresponding product was obtained with KF/CP catalysts (Table 1, entry 5). In homogeneous reactions, equimolar amounts of homogeneous analogues of the corresponding solid bases were employed.

Effectively, less than 10% product was obtained with CP even after 100 min (Table 1, entry 1) and no detectable product formation was observed with KF or NaF (entries 2 and 3). These results provide evidence that the KF/CP is the best catalyst and that the high activity is attributed to the high dispersion of KF on CP support.

A series of chalcone derivatives were investigated in the Michael reaction with malononitrile using optimal conditions. Most substrates underwent the reaction smoothly and gave the corresponding products in high yield (Table 2) except in the case of nitromethane (Table 2, entry 13). The electronic property of the substitution at the aromatic ring  $R^1$  as well as  $R^2$  had no obvious effect on yield of reaction (Table 2, entries 1–16). Thus, the activity of KF/CP was higher than KF [7],  $Al_2O_3$  [8], KF/ $Al_2O_3$  [9], and Mg–Al hydrotalcite [10] and is comparable with Mg–Al-*O-tert*-Bu hydrotalcite [11], ytterbium triflate hydrate [12] and ionic liquids [13,14].

Among the solvent used, methanol, ethanol and hexane, the first was the best. No by-products resulting from the undesirable 1,2-addition and/or bis-addition side reactions were observed.

The negatively charged fluoride moiety abstracts the proton from activated methylene to generate a carboanion stabilized at the potassium surface. Consequently, the C–C bond formation is accelerated, and the final product is obtained after protonation of the resulting enolate.

In summary, we have shown that a new heterogeneous solid base KF/CP is a highly efficient catalyst for the selective 1,4-addition reaction. The main advantages of the described procedure are: facile handling of the solid base; greater reaction rate and quantitative yields with a variety of substrates tested; elimination of further product purification, and the use of inexpensive and available solid support which made an economic process.

#### General procedure

A 50 mL flask was charged with chalcones (1 mmol), malononitrile (1 mmol), KF/CP (30 mg) and methanol. The mixture was stirred at 45 °C for appropriate time until completion of the reaction, as monitored by TLC. Then the

Table 1  
Comparison of KF/CP with several heterogeneous catalysts in the synthesis of products **3a** by Michael addition.

| Entry | Catalyst | Time (min) | Yield (%) |
|-------|----------|------------|-----------|
| 1     | CP       | 100        | <10       |
| 2     | NaF      | 80         | NR        |
| 3     | KF       | 80         | NR        |
| 4     | NaF/CP   | 20         | 75        |
| 5     | KF/CP    | 12         | 97        |

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