Pergamon

Tetrahedron Letters, Vol. 38, No. 10, pp. 1721-1724, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00180-9

# Rare-earth (RE) Exchanged NaY Zeolite Promoted Knoevenagel Condensation

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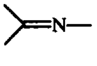
*Key Words*: Knoevenagel condensation; Rare earth-exchanged NaY zeolites; Active methylene compounds; Environmentally-benign; Recyclable catalysts.

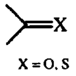
*Abstract*: Knoevenagel condensation is assisted by rare-earth exchanged NaY zeolites wherein various functionalized arylaldehydes react readily with active methylene compounds to produce corresponding olefinic products.

Zeolite catalysts,[1] with their supercages and channels of defined sizes, have received considerable attention in the last decade for organic transformations.[2-6] These 'molecular level microreactors' have been used for the synthesis of intermediates and fine chemicals.[2-4] In the petrochemical industry and for some titanium silicate-catalyzed[4] oxidative protocols, these materials are competing with conventional reagents especially for small and medium size organic substrates.

In continuation of our ongoing effort to develop newer environmentally benign methods for chemical transformations, we decided to investigate the effect of cation exchanged Y-type zeolites in reactions of systems **A-D**. The earlier known work in this area is restricted only to the reactions of imines (**A**) with nitromethane in the presence of RE(70%)NaY zeolite[5] and carbonyl compounds (**B**; X=O)[6] with active methylene compounds utilizing NaGeX (germanium aluminate)[6a] and alkaline exchanged sepiolites (magnesium silicates).[6b] However, the zeolite-catalyzed reactions of thiocarbonyl systems (**B**; X=S), azo-compounds (**C**), or their cyclic counterparts (**D**) have not been explored.

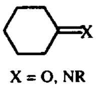


**A**



**B**

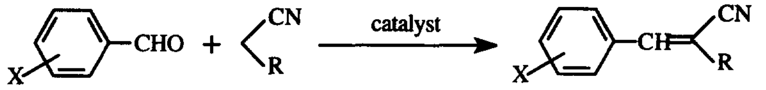
**C**



**D**

Herein, we report our preliminary results on rare-earth (RE) exchanged NaY zeolite-assisted Knoevenagel condensation (**B**; X=O), a reaction that was originally performed in the presence of amines,[7] and has since been revisited[8] using other bases,[9] Lewis acids $ZnCl_2$,[10] $TiCl_4$/base[11] and solid support catalysts such as $Al_2O_3$,[12] $AlPO_4$-$Al_2O_3$,[13] and clays.[14]

Preliminary experiments with a zinc-exchanged NaY zeolite [Zn(70%)NaY] for the condensation of benzaldehyde with malononitrile (Eqn. X=H, R=CN; Table 1, entry 4) produced the desired olefin in 59% yield and with more than 80% conversion of aldehyde.



(Eqn.)

Where X = H, *p*-Br, *p*-$NO_2$, *p*-OH and *m*-OMe
R = CN, $CO_2Et$, $CONH_2$

Consequently, a systematic and comparative study of this reaction has been undertaken with various other cation-exchanged NaY catalysts (Table 1). Two of the catalysts,[15a] La(70%)NaY and Ce(70%)NaY, afforded moderate yields; however, rare-earth (RE) exchanged NaY,[5,15] is found to be the ideal zeolite for this condensation in terms of yields, mass balance and purity of the product (Table 1, entry 7).

**Table 1**: The condensation of benzaldehyde with malononitrile in presence of zeolites.[a]

| Entry | Catalyst | Conditions (Temp./Time) | Yield (%)[b] | Mass balance (%) |
|---|---|---|---|---|
| 1 | H-ZSM-5 | 60 °C, 17 h | 08 | 82 |
| 2 | CaY | 60 °C, 14 h | 18 | 78 |
| 3 | NaY | 60 °C, 14 h | 21 | 73 |
| 4 | Zn(70%)NaY | 60 °C, 08 h | 59 | 85 |
| 5 | La(70%)NaY | 60 °C, 08 h | 65 | 80 |
| 6 | Ce(70%)NaY | 60 °C, 09 h | 67[c] | 78 |
| 7 | RE(72%)NaY[d] | 20 °C, 12 h | 78 | 90 |

a) All the reactions carried out in acetonitrile with 1:1.3 equiv. of benzaldehyde and malononitrile with 50 wt% (of aldehyde) catalyst. b) Isolated and unoptimized yields. c) Average yield of two cycles. d) RE = Rare earth cation-exchanged NaY.[15]

Briefly, the preparation of the rare-earth (RE) exchange[15] catalyst involves the treatment of zeolite NaY[1] with aqueous rare-earth chloride solution (prepared using double distilled and deionized water with pH adjusted to 5.0) at 95 °C for 8 h. After cooling to room temperature, the exchanged catalyst is filtered off and washed with water. The percentage of $Na^+$ exchange is determined (35%) by conventional gravimetric analysis of the aqueous filtrate and this procedure is repeated twice that results in maximum exchange of 72%. The RE(72%)NaY is dried at 120 °C for 4 h and its crystalline structural integrity is discerned by X-ray analysis.[15a]

Aromatic aldehydes bearing a variety of functional groups namely *p*-bromobenzaldehyde, *p*-nitrobenzaldehyde and vanillin are reacted with active methylene compounds such as malononitrile, ethylcyanoacetate and 2-cyanoacetamide in the presence of freshly activated RE(72%)NaY. These reactions lead to completion in 8-12 h at 20-60 °C to produce the olefinic products in 62-87% yield (Table 2).[16] The reaction with more acidic malononitrile proceeds at 20 °C, but ethylcyanoacetate and 2-cyanoacetamide require elevated temperature. The reaction conditions and the corresponding yields of these three active methylene species suggest their reactivity order is: R = CN > $CO_2Et$ > $CONH_2$. Nitrobenzaldehyde, bearing a strong electron withdrawing group, afforded the highest yield relative to other aldehydes. The enhanced reactivity is not only due to a conventional electron withdrawing nature of the nitro group but it also probably due to the interaction between the cations present in the supercages and the oxygen of the nitro group.[17] Initially, vanillin bearing an additional meta substituent has afforded poor yield as well as low mass balance perhaps due to the size limitations.[18,19] However, an improved extraction procedure, warming the spent zeolite with methylene chloride, retrieved additional product thereby improving the yield and mass balance (Table 2, entry 10-12). The turnover frequency (TOF), measured as the molar ratio between the olefinic product formed and the rare-earth ions present in the supercages of the catalyst, is about 6 times higher for the RE(72%)NaY than for the mixture of rare-earth chlorides.[19a]

**Table 2:** The RE(72%)NaY zeolite-assisted Knoevenagel condensation.[a]

| Entry | Aldehyde | R | Conditions (°C, t/h) | Mass balance (%) | Yield (%)[b] | m.p. (°C) (lit. ref.) |
|---|---|---|---|---|---|---|
| 1 | Benzaldehyde | CN | 20, 12 | 90 | 78 | 83[13] |
| 2 | | $CO_2Et$ | 60, 08 | 82 | 70 | 50[13] |
| 3 | | $CONH_2$ | 60, 12 | 80 | 62 | 121[10] |
| 4 | *para* - Bromobenzaldehyde | CN | 20, 08 | 90 | 85 | 164[20] |
| 5 | | $CO_2Et$ | 60, 12 | 90 | 82 | 97[20] |
| 6 | | $CONH_2$ | 60, 18 | 84 | 79 | 219[20] |
| 7[c] | *para* - Nitrobenzaldehyde | CN | 20, 10 | 95 | 87 | 159[13] |
| 8 | | $CO_2Et$ | 60, 08 | 85 | 86 | 169[13] |
| 9 | | $CONH_2$ | 60, 08 | 78 | 82 | 237[20] |
| 10[d] | Vanillin | CN | 60, 12 | 84 | 74 | 131[10] |
| 11[d] | | $CO_2Et$ | 60, 12 | 87 | 71 | 113[10] |
| 12[d] | | $CONH_2$ | 60, 12 | 81 | 68 | 203[10] |

a) Reactions carried out in acetonitrile under dry conditions using freshly activated catalyst. b) Isolated and unoptimized yields. c) Catalyst is recycled three times after reactivation. d) Products are isolated by extraction in hot methylene chloride.

It is pertinent to speculate on the role of multicatalytic active sites present inside the supercages. The basic site abstracts the proton from the active methylene compounds; whereas the Lewis acidic site could be responsible for generating the partial positive charge on the carbonyl carbon by coordinating with its oxygen, and thereby facilitating C-C bond formation. Subsequent transfer of a proton followed by dehydration affords the final product. The overall condensation is presumably facilitated *via* the electrostatic interactions between the exchanged cations and the included organic guests.[17]

In conclusion, we have demonstrated the general utility of rare-earth exchanged NaY zeolites in the Knoevenagel condensation. The reaction of carbonyl substrates and active methylene compounds using RE(72%)NaY zeolite produces the corresponding olefinic products in good yields. The attractive features of our environmentally-benign approach are the recyclable nature of these catalysts and their ease of separation from the reaction mixtures.

## ACKNOWLEDGMENT

We thank Dr. S. Sivasanker NCL, Pune, India for the supply of NaY zeolite and Texas Advanced Research Program (ARP) in Chemistry (Grant # 003606-023) and Texas Regional Institute for Environmental Studies (TRIES) under Contract from U. S. Army Research Office (Grant # DAAH 04-93-G-0505) for the generous support.

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(*Received in USA* 23 *December* 1996; *accepted* 22 *January* 1997)