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Zeolite Mediated Michael Addition of 1,3-Dicarbonyl Compounds and Thiols.

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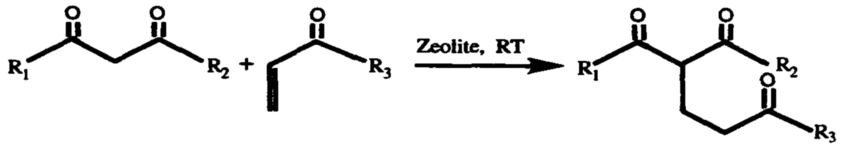
Abstract : Zeolites, an environmentally attractive solid catalyst, proves to be an efficient catalyst for Michael addition of several 1, 3-dicarbonyl compounds and thiols as donors with methyl vinyl ketone, acrolein and methyl acrylate as acceptors without any solvent are described. © 1997 Elsevier Science Ltd.

Zeolites as catalyst have recevied considerable attention in the last decade due to their characteristic properties such as shape selectivity, thermal stability, acidic and basic nature.[1] The utility of zeolites as selective adsorbents and as cracking catalysts in petroleum industry has been known for many years.[2] However, their application in general organic synthesis has not been fully explored. The Michael reaction is one of the efficient methods for effecting carbon-carbon bond formation and has wide synthetic applications in organic synthesis. [3] Traditionally, these reactions are catalyzed by strong bases such as alkali metal alkoxides and hydroxides.[4] The limitation of these strong bases in these reactions are mainly the formation of undesirable side products by polymerization, bis-addition and self-condensations. In recent years various catalysts such as phase transfer catalysts,[5] transition metal complexes, [5] $SnCl_4$, [5] $TiCl_4$, [5] lanthanides, [6] LiI, [7] CsF, [8] clay and alumina [9] has been used to effect carbon-carbon bond formation. Hitherto no report is available in the literature in which a zeolite is employed to promote the Michael reaction.

As a part of our continuing efforts to explore the novel utilities of zeolite mediated reactions,[10] we wish to report here a mild, heterogeneous catalytic method for the Michael reaction of several 1,3-dicarbonyl compounds and thiols with methyl vinyl ketone (MVK), acrolein and methyl acrylate (MA). The hydrothermal synthesis of zeolites[11] were carried out as follows : About 6.05 g of NaOH (50 wt %



solution) was added slowly under stirring to 7.26 g of sodium aluminate dissolved in 25 mL of water. A solution of 7.06 g of 15-Crown-5-ether in 15.0 mL of water was added under stirring to 77 g of silica solution. Then the sodium aluminate-sodium hydroxide mixture was added slowly to the silica solution and stirred for 10 min. The reaction mixture was transferred to a polypropylene bottle and kept in an oven at 110 °C for 12 days after an ageing period of 2 days. The Y-Zeolite crystallized was filtered, washed and dried at 100 °C for 5 h.

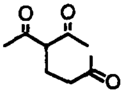
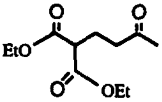
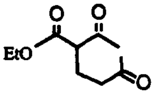
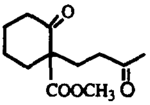
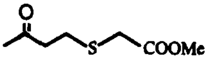
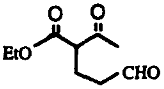
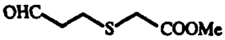
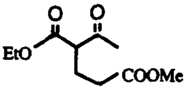
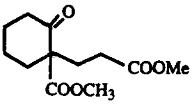
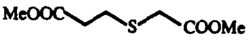
About 150 mL of tetraethylammonium hydroxide solution (35 wt % in water) was concentrated in a rotavapor to 55 mL. This solution was added under stirring to 2.13 g of sodium aluminate dissolved in 24 mL water followed by 52.2 g tetraethyl orthosilicate. The reaction mixture was poured into a polypropylene bottle and shaken periodically. After 20 min. the hot gel mixture was cooled down under flowing water and allowed to stay at room temperature for 40 min. Then the gel was transferred into a stainless steel autoclave and crystallization occurred in 12 days at 110 °C under static conditions. The zeolite beta sample was filtered, washed and dried at 100 °C for 5 h. Prior to use, the zeolites were activated at 500 °C for 5 h in presence of air.

In a typical procedure, acetylacetone (1 mmol) was stirred with NaY-Zeolite (1 g) at room temperature for 15 min. under nitrogen atmosphere after which MVK (1 mmol) was added and stirring was continued until the completion of the reaction, as monitored by TLC. The zeolite was washed with methanol (3 x 25 mL) to extract out the Michael adduct from the channels of zeolite. Removal of the solvent followed by the purification of the residue by passing through a short column of silica gel using chlorofom as eluent affords the product in 92% yield.

As shown in Table 1, several structurally varied diketones and thiols underwent clean, fast and efficient Michael addition with methyl vinyl ketone, acrolein and methyl acrylate over NaY-Zeolite and Na-Zeolite beta in high yield. Interestingly, the reaction was slow when it was conducted in presence of solvents like 1,2-dichloroethane or THF. The reasons for the efficiency of the process on the zeolite are yet to be explored. The reactions were usually carried out at room temperature, although in two cases where acrolein is involved, lower temperature furnished better yields. When HY-Zeolite was used instead of NaY-Zeolite the desired Michael adduct formation was low and the polymerization of Michael acceptor was the main reaction. One of the major advantages of zeolite over other solid catalysts for Michael addition is its easy set-up and work-up procedure and reuse of the catalyst after activation.

In conclusion, the salient features of this methodology are: (i) mild reaction conditions, (ii) ease of work-up, (iii) high yield of products, (iv) recycling of the catalyst and (v) the reaction involves non toxic and inexpensive materials.

Table 1 Zeolite mediated Michael addition of 1,3-dicarbonyl compounds and thiols.

Donor	Acceptor	Time	Product[a]	m.p/b.p(°C)	Yield[b] (%)	
					NaY-Zeolite	Na-Zeolite beta
Acetylacetone	MVK	20 min.		98(0.2mm)[5b]	82	80
Diethylmalonate	MVK	3 h		107(0.2mm)[5b]	78	79
Ethylacetoacetate	MVK	15 min.		127(0.45mm)[5b]	81	84
Methyl 2-oxocyclo-hexane carboxylate	MVK	15 min.			80	77
Methylthioglycolate	MVK	15 min.			76	70
Ethylacetoacetate[c]	Acrolein	20 min.			80	79
Methylthioglycolate[c]	Acrolein	20 min.			71	75
Ethylacetoacetate	MA	3 h			81	78
Methyl 2-oxocyclo-hexane carboxylate	MA	3 h			74	72
Methylthioglycolate	MA	2 h			71	68

[a] all products were characterized by their IR, ^{1}HNMR and Mass spectra. [b] Isolated pure products. [c] Reactions were carried out at 0 °C.

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