Allylation of Aldehydes Catalyzed by Zeolites under Liquid Phase

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Dealuminated zeolite-Y exchanged with rare earth metals (RE-Y) is found to catalyze the allylation of different aldehydes using allyltrimethylsilane to afford the corresponding allylic compounds in moderate to good yields by refluxing in nitromethane.

Allylation of aldehydes with allyltrialkylsilanes is one of the most important carbon–carbon bond forming reactions in organic synthesis. This reaction is generally effected over traditional Lewis acids such as $SnCl_4$, $TiCl_4$, $AlCl_3$, $NbCl_3$, and indium (III) chloride.[1–4] Several rare earth triflates like $Sc(OTf)_3$, $Yb(OTf)_3$, $Zr(OTf)_4$, and $Hf(OTf)_4$ have also been investigated under the homogeneous conditions.[5–8] However, most of these conventional Lewis acids are corrosive as well as moisture sensitive, and also the metal triflates are very expensive. Furthermore, there is intense research around the world to replace these conventional catalysts by greenish, environmentally safer heterogeneous catalysts. Although several catalysts are reported for the allylation of aldehydes under homogeneous condition, there is no report over the heterogeneous catalyst under the liquid-phase.

Microporous aluminosilicates (zeolites) have been extensively studied for the vapor-phase carbon–carbon bond formation reactions by replacing the conventional Fridel–Crafts alkylation catalysts for the production of a variety of fine chemicals in industry. The regenerability as well as tunable acidity of zeolites makes them as a potential catalyst for various chemical transformations. Here we report, for the first time the utility of rare earth metals exchanged zeolite-Y for the successful reaction of allyltrimethylsilane with different aldehydes under optimum reaction conditions.

Lewis-acidity of zeolite-Y was increased by modifying the Na-Y through exchange with rare earth solution according to the following two different methods. In the first method, Na-Y was first converted into NH_4 form by exchange with 2 M ammonium acetate solution at 80 °C for 24 h. Then the NH_4-Y was stirred with rare earth solution at 90 °C and this procedure was repeated three times to maximize the exchange of rare earths cations (method I). In the second method, the NH_4-Y was subjected to dealumination with $(NH_4)_2SiF_6$ (1 N solution, 10 mL) slowly under 90 °C for 24 h. Then, the dealuminated zeolite was exchanged with rare earth solution as mentioned above (method II). Similarly, mordenite and β were also prepared by adopting similar procedure of the method II.

In a typical allylation reaction, 10 mmol of aldehydes and 10 mmol of allyltrimethylsilane were mixed in *dry* nitromethane in a round bottom flask, to which 30 wt% (with respect to aldehyde) of the catalyst was added. Then the reaction mixture was refluxed under vigorous stirring using magnetic bar for 18 h.

After the reaction, the mixture was quenched with aqueous $NaHCO_3$ and extracted with diethyl ether (3×15 mL). The combined extracts were dried over anhydrous sodium sulphate, and the solvent was removed in rotary evaporator under reduced pressure. The products were extracted with column chromatography and identified with GC, GC-MS splitting pattern, and ^{1}H NMR.

Table 1 exhibits the activity of different modified catalyst for the reaction between benzaldehyde and allyltrimethylsilane (Scheme 1). The catalyst prepared by successive dealumination followed by rare earth exchange, shows the best activity (Entry 1) than that prepared without dealumination step (Entry 2). The poor activity observed over H-Y (Entry 3) indicates that Brønsted acid sites may less favor this reaction. Furthermore, mild basic Na-Y did not show any activity under similar condition (Entry 4). Thus the increased activity of the RE-Y may possibly due to the creation of Lewis acidic trigonally coordinated aluminum species by dealumination coupled with rare earth metal exchange. However, other modified catalysts such as RE-mordenite and RE-β, (Entries 5 and 6) exhibit slightly less

Table 1. Activity of various modified aluminosilicates over allylation of benzaldehyde[a]

Entry	Catalyst	Solvent	SiO₂/Al₂O₃ ratio	Yield, %
1	RE-Y[b]	Nitromethane	11.5	52.0
2	RE-Y[c]	Nitromethane	2.5–3.0	30.0
3	H-Y	Nitromethane	2.5–3.0	16.0
4	Na-Y	Nitromethane	2.5–3.0	Nil
5	RE-mordenite	Nitromethane	22.5	43.0
6	RE-β	Nitromethane	60.0	35.0
7	RE-ZSM-5	Nitromethane	80	12.0
8	RE-Y[b]	Acetonitrile	11.5	50.0
9	RE-Y[b]	THF	11.5	21.0
10	RE-Y[b]	Dichloromethane	11.5	17.0

[a]Reaction conditions: 10 mmol of benzaldehyde, 10 mmol of allyltrimethylsilane, 20 mL of dry solvent, 30 wt% of catalyst, temperature 90 °C, reaction time 18 h.
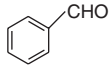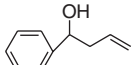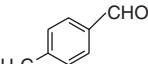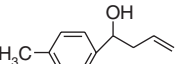[b]Catalyst prepared by dealumination followed by rare earth exchange.
[c]Catalyst prepared by direct ion-exchange with rare earth solution.
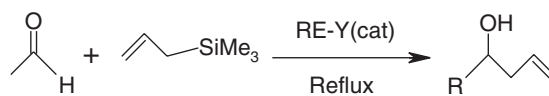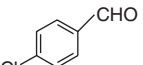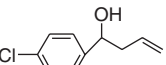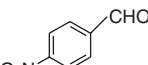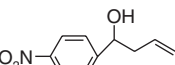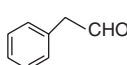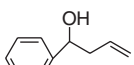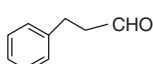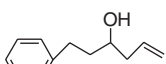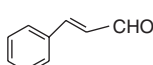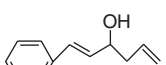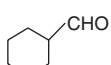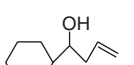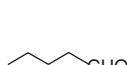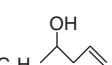
Scheme 1.

Table 2. Allylation of various aldehydes with allyltrimethylsilane over RE-Y[a]

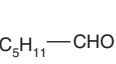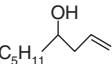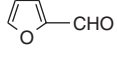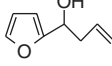| Entry	Aldehydes	Products	Yield[b], %
1			52.0
2			55.0
3			48.0
4			45.0
5			48.0
6			47.0
7			40.0
8			70.0
9			65.0
10			59.0
11			51

[a]Reaction conditions: 10 mmol of aldehyde, 10 mmol of allyltrimethylsilane, 20 mL of dry nitromethane, 30 wt% of RE-Y, temperature 80 °C, reaction time 18 h.
[b]Isolated yield by column chromatography.

activity than that observed over RE-Y. The decreased activity over RE-ZSM-5 (Entry 7) may partly be attributed to diffusion limitation exerted at the medium pore. Among the various sol-vents studied for this reaction, nitromethane shows the best activity. Therefore, RE-Y/nitromethane was chosen as the superior catalytic system for further study.

The allylation of a variety of aldehydes such as aromatic, aliphatic, and cyclic aldehydes is exhibited in the Table 2. Entries 1-4 show the activity of benzaldehyde and substituted benzaldehyde; the presence electron withdrawing groups decreases the activity marginally and attributed to the decreased electrophilicity of carbonyl carbon. Bulky aldehydes such as 2-phenyl acetaldehyde, 3-phenylpropinaldehyde, and cinnamaldehyde (α, β-unsaturated aldehyde) afford moderate yields (Entries 5-7). Cyclohexanecarboxaldehyde (Entry 8) as well as open-chain aldehydes exhibits the best activity (Entries 9 and 10) than the aromatic aldehydes. The aldehyde with heteroatom (Entry 11) also undergoes smooth allylation to afford the corresponding allylic product in good yield. It is important to mention that in all the aforementioned reactions, the unreacted aldehydes were isolated and no side products were formed. Thus the scope of this catalyst is evident from the above summarized results. Most importantly, the use of heterogeneous catalyst over its homogeneous counterpart offers several advantages such as environmental safety and easy separation. In short conclusion, the modification of zeolite Y by dealumination followed by ion exchange with rare earth metals leads to high activity in the liquid-phase carbon–carbon bond formation reaction between different aldehydes and allyltrimethylsilane.

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