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Ti-exchanged ZSM-5 as heterogeneous catalyst for allylation of aldehydes with allyltributylstannane

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ABSTRACT

Titanium exchanged ZSM-5 catalyst has been prepared by treating an aqueous solution of titanium (IV) chloride with ZSM-5. The supported catalyst has been explored as effective and reusable catalyst for allylation reaction of aldehydes with allyltributylstannane. The new catalytic system promotes efficiently the allylation reaction in toluene condition to produce homoallylic alcohols in high yield.

ZSM-5 is one of the widely applied solid acid catalysts in industry for various synthetic transformations.[1] In the past decades, significant efforts have been undertaken to design zeolite catalysts by incorporating certain transition metals in zeolite framework for task specific applications.[1] In this regard, TS-1 and VS-1 were found to be very successful zeolite catalysts for various oxidative transformations.[2] However, study on the titanium containing ZSM-5 made by post synthetic modification using ion-exchange method has received scant attention in the literature.

The addition of allyl metal reagents to aldehydes is an important method for formation of carbon–carbon bond.[3] The utility of this method has been demonstrated by numerous applications in organic synthesis.[3] Allyltributylstannane is one of the most common reagents used for the synthesis of homoallylic alcohols. In recent years, several Lewis acids, especially metal Lewis acids, or transition metal complexes have been utilized extensively to catalyze this transformation including those based on B,[4] Sn,[5] Ti,[6] Zr,[7] Rh,[8] Re,[9] Sc,[10] Gd,[11] Ce,[12] Pd,[13] Ag[14] and Cu.[15] However many methods using Lewis acids require strictly anhydrous conditions. Although rhenium complex[9] or scandium triflate[10] are very effective as air-stable and water-tolerant catalysts for allylation reaction, these catalysts are expensive. Moreover, the rhenium complex was found to be effective for allylation reactions only at higher temperature. Cerium (III) chloride ($CeCl_3{\cdot}7H_2O$) in combination with NaI, has been used as a stoichiometric promoter for the allylation of various aldehydes with allyltributyltin.[12] The major drawback of this method is the use of a stoichiometric amount of the promoter to effect the reaction. Several Pd-complexes[13] and silver triflate[14] has been reported by many researchers. However, palladium and silver compounds are expensive and in many cases the method requires stringent dry reaction conditions at low temperature. We have also reported a method for the synthesis of homoallyl alcohols using CuI as catalyst.[15] However, this catalyst is effective only in homogeneous condition. Although several homogeneous metal complexes have been examined, a very limited effort has been made to use heterogeneous catalyst for the allylation reaction. Wang[16] may be the first to report a heterogeneous resin supported catalyst for allylation of aldehyde with tetraallyltin. But they have applied the method only in the case of hexanal and no detail investigation was made to generalize the procedure with other aldehydes. Later, Portnoy[17] reported the preparation of pincer bis(oxazolinyl)phenyl ligands on polymer support for rhodium catalyzed allylation reaction of various aldehydes with allyltributylstannane. Very recently, Zhao and Li reported a new method for homoallylic alcohol synthesis using a polymer-supported sulfonamide of *N*-glycine as catalyst.[18] As a part of our investigations on various allylation reactions,[15,19] we report herein, for the first time, the use of a heterogeneous titanium catalyst viz. Ti-exchanged ZSM-5 for the synthesis of homoallylic alcohols (Scheme 1).

Since an extensive study has already been carried out for allylation of aldehydes using various titanium complexes,[6] we sought to develop a heterogeneous titanium catalyst by post synthetic modification of ZSM-5. Initially ZSM-5 samples were prepared by following a procedure reported in the literature.[20] Formation of

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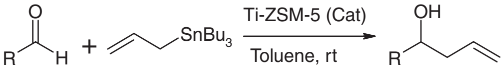


Scheme 1. Allylation of aldehydes using Ti-ZSM-5 as catalyst.

ZSM-5 was confirmed by comparing the XRD and IR spectra with standard data.[21] The X-ray diffraction patterns show high crystallinity of the ZSM-5 samples. Morphology of the ZSM-5 samples was further examined using scanning electron micrograph. The Si/Al ratio of the ZSM-5 sample was determined from EDX analysis and it was found to be 84.

The Ti-exchanged ZSM-5 was made by stirring ZSM-5 in an aqueous solution of $TiCl_4$ at room temperature. Different samples of Ti-ZSM-5 were prepared by varying the amount of $TiCl_4$. XRD-patterns confirm the crystalline nature of the Ti-ZSM-5 samples (Fig. 1).

Morphology of the Ti-ZSM-5 samples was also analyzed by using SEM. Titanium content of the Ti-exchanged ZSM-5 samples was determined by EDX analysis. Analysis of the SEM pictures revealed that there is a significant impact of titanium exchange on the crystallinity of the parent ZSM-5 samples. We observed that the catalyst retains typical ZSM-5 morphology when titanium loading is about 0.4 wt % (Fig. 2). However, slight deformation of the structure was observed in case of Ti-ZSM-5 samples having 1.34 wt % of titanium. Further increase of Ti-content led to deformation of crystalline structure of the ZSM-5 sample.

After confirming the structure and morphology of the as prepared Ti-ZSM-5 samples, we intended to test the efficacy of the catalyst for allylstannation of aldehyde. Initially, a systematic study on the synthesis of homoallylic alcohols was carried out using 4-chlorobenzaldehyde as substrate. In a typical reaction, allyltributylstannane (1.05 mmol) was added to a mixture of 4-chlorobenzaldehyde (1 mmol) and Ti-ZSM-5 containing 0.4 wt % of titanium as catalyst (10 wt % based on aldehyde) in acetonitrile at room temperature (Table 1). Reaction at room temperature in acetonitrile failed to yield the desired product after 24 h of reaction. When, the reaction was carried out in benzene, corresponding homoallyl alcohol was obtained in 78% isolated yield after 36 h of reaction at room temperature. We have also tested the catalytic efficiency of the parent ZSM-5 sample under the same reaction condition. We found that the rate of the reaction is very slow in the presence of ZSM-5 and the reaction furnished 28% yield of the product after 48 h of reaction. Thereafter, a comparative study was carried out for evaluation of the catalyst using different solvents such as dichloromethane, toluene and diethylether (Table 1). The reaction took relatively longer time to occur in ether, whereas, the reaction did not proceed in dichloromethane. Use of toluene gave slightly lower yield than in benzene. Thereafter, we carried out the experiment in toluene, increasing the amount of catalyst. Although the reaction gives marginally better yield in benzene, we have chosen toluene as solvent due to its nonhazardous nature. It was found that the use of 35 wt % of the catalyst is sufficient to drive the reaction to completion in 10 h in high yield.

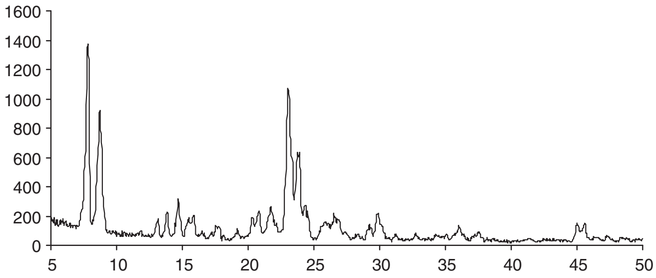


Figure 1. XRD-pattern Ti-ZSM-5 (0.4 wt % Ti).

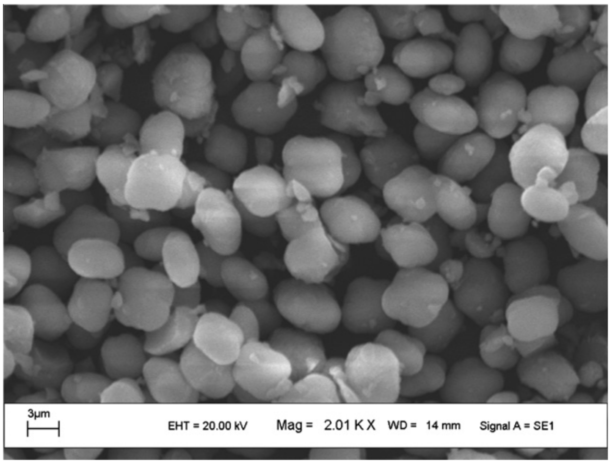


Figure 2. SEM picture of Ti-ZSM-5 (0.40 wt % of Ti).

After evaluating the most suitable condition for allylation reaction, we carried out a comparative investigation of the catalytic efficiency of the Ti-ZSM-5 samples (0.4, 1.34, and 15.6 wt % of titanium). While the Ti-ZSM-5 with 1.34 wt % of Ti produced lower yield of corresponding homoallyl alcohols, the deformed Ti-ZSM-5 sample with 15.6 wt % of titanium was not at all catalytically active for this reaction. Deformation of ZSM-5 structure due to higher amount of titanium exchange may be the reason for decrease in reactivity of the catalyst.

We have further extended the procedure in case of different aldehydes, the results are summarized in Table 2. The reaction was carried out using 1 mmol of aldehyde, 1.05 mmol of allyltributylstannane, 35 wt % of Ti-ZSM-5 in toluene (1 mL) at room temperature.[22] Both aromatic and aliphatic aldehydes underwent homoallylation with high yields. Substituted benzaldehydes such as 4-chloro-, 4-fluoro- 4-nitro-, 4-methoxy-, 4-methyl-, and 4-bromo- were examined under the optimized reaction conditions (entries 2–7). Aldehyde possessing electron withdrawing substituents such as nitro group produced lower yield of corresponding homoallylic alcohol. We observed that aldehyde possessing methoxy substituent gave slightly lower yield, which may be due to poor defusibility of the substrate. Under similar conditions naphthaldehyde also underwent allylation reaction to the corresponding homoallylic alcohol in 80% yield (Table 2, entry 8). We have successfully extended the procedure to the aliphatic aldehyde octanal

Table 1
Synthesis of homoallylic alcohols from benzaldehyde under various conditions[a]

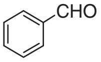
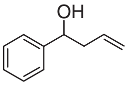
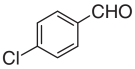
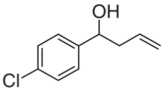
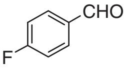
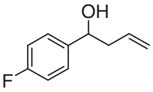
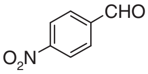
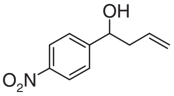
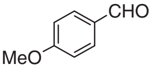
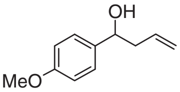
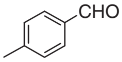
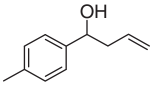
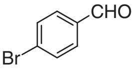
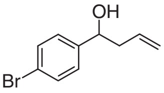
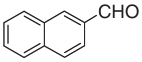
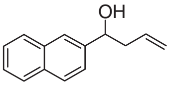
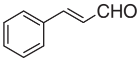
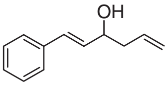
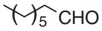
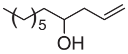
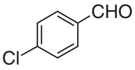
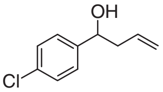
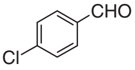
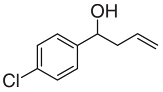
Sl. No.	Catalyst[b]	Catalyst amount (wt %)	Solvent	T (h)	Yield[c] (%)
1	ZSM-5	10	MeCN	24	NR
2	Ti-ZSM-5	10	MeCN	24	NR
3	Ti-ZSM-5	10	Benzene	36	78
4	ZSM-5	10	Benzene	48	28
5	Ti-ZSM-5	10	Ether	36	56
6	Ti-ZSM-5	10	DCM	36	NR
7	Ti-ZSM-5	10	Toluene	36	72
8	Ti-ZSM-5	20	Benzene	24	77
9	Ti-ZSM-5	20	Toluene	24	75
9	Ti-ZSM-5	30	Toluene	12	78
9	Ti-ZSM-5	35	Toluene	10	83
9	Ti-ZSM-5	40	Toluene	10	82

[a] Reaction conditions: chlorobenzaldehyde (1 mmol), allyltributylstannane (1.05 mmol), solvent (1 mL), rt.

[b] Ti-ZSM-5 samples with 0.4 wt % of Ti was used.

[c] Isolated yield after chromatographic purification. NR: no reaction.

Table 2
Synthesis of homoallylic alcohols using Ti-ZSM-5 catalyst

Sl. No.	Aldehyde (a)	Product (b)	*T* (h)	Yield[a]
1			10	81
2			10	83
3			8	85
4			12	72
5			8	79
6			8	83
7			10	85
8			12	80
9			16	74
10			16	71
11[b]			10	81
12[c]			10	82

[a] Isolated yield after chromatographic purification.
[b] Recovered catalyst was reused (1st run).
[c] Recovered catalyst was reused (2nd run).

and an aldehyde containing a double bond viz. cinnamaldehyde (entries 9 and 10). All compounds were characterized by comparing the NMR and IR values with those reported in the literature. Reusability of the catalyst was examined in case of 4-chlorobenzaldehyde. The recovered catalyst was dried under vacuum oven at 60 °C for 6 h before use. The catalyst could be reused successfully for two times without significant loss of activity (Table 2, entries 11 and 12).

Ti-exchanged ZSM-5 was synthesized by treating ZSM-5 with an aqueous solution of $TiCl_4$ at room temperature. The newly developed catalyst was found to be an active heterogeneous catalyst for allylation of aldehyde with allyltributylstannane. Ti-ZSM-5 with 0.4 wt % of titanium was found to be more active catalyst than that containing 1.34 wt % of titanium.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.03.056.

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22. *Typical procedure*: To a mixture of aldehyde (1 mmol) and Ti-ZSM-5 (0.35 mmol) in toluene (1 mL) allyltributylstannane (1.05 mmol) was added and the reaction was stirred for appropriate time (TLC). After completion of the reaction, catalyst was filtered off and the solvent was evaporated to get the crude product. The crude product was purified by column chromatography over silica gel (230–400 mesh) using petroleum ether–ethyl acetate mixture as eluent.