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Selective Conversion of Nitroalcohols into Nitroolefins over Zeolite under Heterogeneous Conditions†

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Various zeolites catalyse the formation of aliphatic, aromatic and heteroaromatic nitroolefins from the corresponding nitroalcohols with high selectivity and yield at optimum reaction temperature.

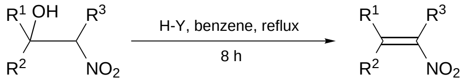
In recent years zeolites have found new applications as heterogeneous acid catalysts for various liquid-phase organic reactions at moderate temperatures.[1] This is primarily due to the advantages associated in the use of solid acids such as easy work-up, eco-friendly nature, regeneration, reusability and their shape-selective nature. Over the last two decades nitroalkenes have been found to be an important intermediate both in industry and in organic synthesis.[2,3] For example, nitroalkenes are commonly used as dienophiles in Diels–Alder reactions[4,5] and they readily undergo addition to a wide range of nucleophiles. In addition, several synthetic transformations of nitroolefins are also known in the literature.[6,7] Usually nitroolefins are prepared by the initial acylation of the hydroxy group of nitroalcohols followed by elimination with sodium acetate in a homogeneous non-catalytic method. Several reagents such as phthalic anhydride,[9] dicyclohexylcarbodiimide,[10] phosphorus pentoxide,[11] pivaloyl chloride,[12] PPh_3–CCl_4–Et_3N[13] and methanesulfonyl chloride–Et_3N[14] are used to effect the dehydration of nitroalcohols to nitroolefins.

In all the above mentioned cases, the separation of the products from the reagents makes the procedure laborious. However, to the best of our knowledge, neither homogeneous nor heterogeneous catalytic methods for the dehydration of nitroalcohols to nitroolefins have been reported.[11,15] Here we report a catalytic dehydration of nitroalcohols to nitroolefins over different zeolites with high conversion and selectivity, at optimum reaction temperature under liquid-phase conditions.

Experimental

The catalysts ZSM-5 and Beta (with Si:Al ratios of 60:1 and 13:1, respectively) were prepared according to published procedures[16,17] using tetrapropylammonium bromide and tetraethylammonium hydroxide respectively as templates. The Na-Y and Na-Mordenite (Si:Al = 2.4 and 5.5, respectively) were obtained commercially from United Catalyst India Ltd and Zeolon, respectively. The above zeolite Na-forms were converted into the H-form by treating 2 g of zeolite with 30 ml of ammonium acetate (1 M) at 80 °C for 3 h. This procedure was repeated in order to ensure the complete exchange of Na^+ by the NH_4 ion. The zeolite was then filtered off, washed thoroughly with deionized water and calcined at 500 °C for 5 h in a flow of dry air to obtain the zeolite H-forms. The RE-Y (rare earth-Y) was obtained by treating Na-Y with a 10% solution of a mixture of rare earth oxide (containing approximately 18 wt% Pr, 48 wt% Nd, the rest being La and a small percentage of other rare earth elements) and calcining at 500 °C for 5 h in a flow of dry air.

In a typical reaction, 3-methyl-1-nitrobutan-2-ol (266 mg, 2 mmol) was taken in 6 ml of dry toluene and then 10 wt% of H-Y zeolite was added and the mixture was azeotropically distilled for 8 h. The progress of the reaction was monitored by TLC using 20% ethyl acetate–light petroleum (bp 35–60°C). The reaction mixture was cooled to room temperature and the catalyst was filtered off. The solvent was removed under reduced pressure and the crude product obtained was purified by column chromatography [100–200 mesh size, 10–15% ethyl acetate–light petroleum (bp 35–60 °C) as eluent] to afford (*E*)-3-methyl-1-nitrobut-1-ene (Table 1, entry 1) as a liquid. All the reaction products were characterised by IR, ^{1}H NMR, ^{13}C NMR, bp and mp. By analogous procedures several other nitroalcohols were converted into nitroolefins over H-Y zeolite (Scheme 1).



R^1, R^2 = alkyl, aryl, heteroaryl, H
R^3 = alkyl, H

Scheme 1

Results and Discussion

Table 1 shows the yield and selectivity of the conversion of various nitroalcohols into nitroolefins over 10% w/w H-Y zeolite. The procedure is general, as aliphatic (entries 1–2), aromatic (entries 3–6) and heteroaromatic (entry 7) nitroalcohols were dehydrated to the corresponding nitroolefins. However, the limitation of this method is that the reaction fails in the case of primary nitroalcohols. It is pertinent to mention that, in all cases, the product selectivity was found to be 100% (for the *E*-isomer) and no side reactions such as nitroolefin polymerisation were observed under the reaction conditions used.

Table 2 shows the effectiveness of various zeolites in the formation of nitrostyrene from 1-phenyl-2-nitroethanol. Zeolites with high Brönsted acid strength such as H-Y (Si:Al = 2.4, large three dimensional 12-member ring pores of 7.4 Å with supercages), H-beta (Si:Al = 13, 12-member ring channels intersecting 6.5 × 5.6 and 7.5 × 5.7 Å), and H-mordenite (Si:Al = 5.5, intersecting 8 and 12-member rings 6.5 × 7.0 and 2.6 × 5.7 Å) induce more conversion (93, 89 and 86 respectively, Table 2, entries 1–3) than zeolites with moderate acidity such as ZSM-5 (Si:Al = 60) with three dimensional intersecting 10-member rings 5.3 × 5.6 and 5.1 × 5.5 Å (Table 2, entry 4). Further, the slightly lower reactivity in the case of RE-Y (Rare earths exchanged zeolite-Y which contain more Lewis acid sites) may be due to the presence of less Brönsted acid sites, which are required for this dehydration reaction. The above results suggest that the reaction is mainly catalysed by Brönsted acid sites rather than the structure of zeolites in the dehydration of 1-phenyl-2-nitroethanol in accordance with previous reports.[10,11] However other solvents seem to exert little influence on the product formation. Entries 8 and 9 show the conversions using benzene (82%) and xylene (78%) as solvent. The catalyst was reused five times without loss of activity, after activating at 400 °C in a flow of air.

In conclusion, we have demonstrated the effective dehydration of nitroalcohols to nitroolefins over zeolite catalysts with high selectivity and good yield.

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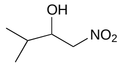
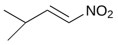
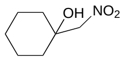
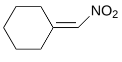
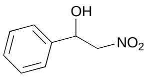
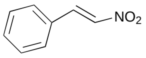
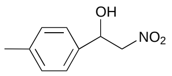
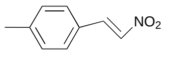
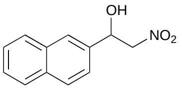
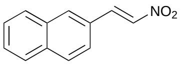
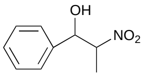
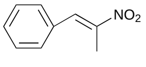
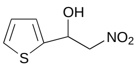
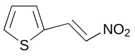
Table 1 Conversion of nitroalcohols into nitroolefins over H-Y (10% w/w) zeolite

Entry	Reactant	Product	Yield (%)[a]	Selectivity (%)[b]
1			73	100
2			81	100
3			93	100
4			82	100
5			85	100
6			81	100
7			93	100

[a]Yields based on recovered starting material. [b]*E*-isomer was determined by the H–H and ^{13}C—H (entry 6) NMR coupling constants.

Table 2 Comparison of various zeolites in the formation of nitrostyrene from 1-phenyl-2-nitroethanol

Entry	Zeolite	Si/Al ratio	Yield (%)[a]	Selectivity (%)
1	H-Y	2.4	93	100
2	H-Beta	13	89	100
3	H-Mordenite	5.5	86	100
4	H-ZSM-5	60	79	100
5	RE-Y	2.4	82	100
6	H-Y	2.4	82	100
7	H-Y	2.4	78	100

[a]Yields based on recovered starting materia. [b]Benzene was used as solvent. [c]Xylene was used as solvent.

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