Conversion of alkenes and alcohols to azides over zeolite-supported sodium azide

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Zeolite-supported sodium azide reagents are versatile catalysts for the conversion of various alkenes and alcohols to the corresponding azides in good yield under mild conditions.

Azides are important precursors of nitrenes or amino compounds and belong to a large family of 1,3-dipoles which undergo cycloaddition to alkenes.[1] While aromatic azides can be obtained by a variety of methods, aliphatic azides are mainly prepared by substitution of alkyl halides, diazo transfer to aliphatic amines or additions to alkenes.[2] In recent years there have been several reports on the use of zeolites for selective organic transformations leading to the synthesis of various fine chemicals.[3–5] Here we report a convenient heterogeneous catalytic methodology for the conversion of alkenes and alcohols to the corresponding azides over zeolite-supported sodium azide reagents (Table 1).

The alkenes and alcohols were purchased from Aldrich and Fluka Chemical Co. and the zeolites (Y-Zeolite, EMT, ZSM-5 and Zeolite beta) were synthesized according to the reported procedure.[6] The Na-zeolites thus obtained were converted to H-zeolites by treatment with aqueous NH_4Cl followed by filtration and activation at 450 °C for 12 h.

Zeolite-supported sodium azide reagents were prepared by dissolving NaN_3 (1 mmol) in 5 ml of deionized water in a 15 ml flask. About 0.75 g of Zeolite were then added and the mixture was stirred for 3 h at room temperature. The mixture was then filtered and washed several times with deionized water. Prior to use the zeolite supported reagents were further dried at 65 °C (5 Torr) for 2 h in a current of air.

The loading amount of NaN_3 (*A* wt%) and the amount of residual water (*B* wt%) on a zeolite supported reagent were defined as shown in eqns. (1) and (2), where *z* is the weight

$$A = 100\ \{z / [z + (1 - \alpha/100)y]\} \quad (1)$$

$$B = 100\{[W - W_o - z - (1 - \alpha/100)y]/(W - W_o)\} \quad (2)$$

of NaN_3 supported, *y* is the weight of zeolite used, α is the wt% of physisorbed water in the zeolite, W_o is the mass of the flask used for the preparation of the zeolite supported reagent and *W* is the mass of the flask containing the zeolite supported reagent after drying at 65 °C (5 Torr) for 2 h. The value of α was determined by thermogravimetric analysis of the zeolite-supported reagent in the temperature range of 30–250 °C. The zeolite supported reagent used for the present study contained 8 wt% loading of NaN_3 and 15 wt% of residual water. Zeolites consist of small uniform pores or channels and the exterior surface area of zeolite is only 0.5–2.0% of the total surface area.[7] Hence most of the supported NaN_3 seems to be finely dispersed inside the pores or channels of zeolite and interacts with water molecules or hydroxy groups on the surface of the zeolite. The role of the small amount of water associated with supported reagents and its reactivity has been discussed by Ando *et al.*[7] Probably the water molecules, as well as the hydroxy groups on the zeolite surface, coordinate to the dispersed NaN_3 to loosen the ion-pairing of $[Na^{+}\cdots N_3^{-}]$, leading to the enhancement in nucleophilicity of the azide anion.

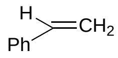
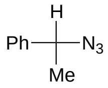
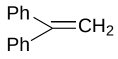
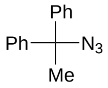
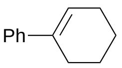
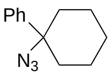
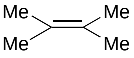
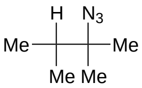
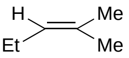
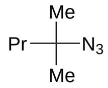
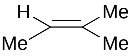
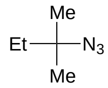
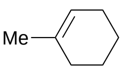
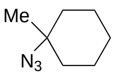
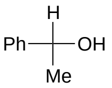
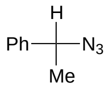
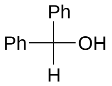
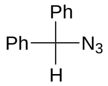
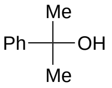
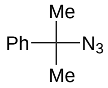
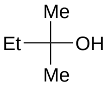
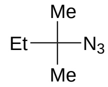
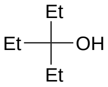
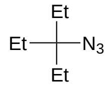
Azide ions (N_3^-) have strong and characteristic IR bands in the region of 2100 cm^{-1} arising from the asymmetric stretching mode while the solid NaN_3 has a diagnostic absorption at 2130 cm^1.[8] A 25 wt% NaN_3 supported zeolite reagent shows a new peak at 2065 cm^{-1} in addition to the parent peak at 2130 cm^{-1}, whereas 8 wt% loaded samples have an absorption peak at only 2065 cm^{-1} (Nujol mull). After zeolite-supported reagents (1 g) were treated with styrene (1 mmol) in the different solvents listed in Table 2 (10 ml) at 70 °C for 2 h, the supported reagents were analysed immediately by IR spectroscopy. It was found that the intensity of the peak at 2065 cm^{-1} decreased dramatically compared with the peak at 2130 cm^{-1} in 25 wt% NaN_3 supported zeolite reagents. In the case of 8 wt% loaded samples, the intensity of 2065 cm^{-1} peak was very low. These results indicate that the azide ions showing the lower frequency peak of 2065 cm^{-1} are much more reactive for the conversion of alkenes and alcohols to the corresponding azides than the azide ions which appeared at 2130 cm^{-1}. Hence, we speculate that the finely dispersed form of NaN_3 shows absorption at 2065 cm^{-1} and the coagulated NaN_3 crystals exhibit absorption at 2130 cm^{-1}. Under the same reaction conditions, the low loading (8 wt%) samples show higher reactivity for the conversion of styrene to 1-azido-1-phenylethane (84%) compared to a 25 wt% loaded samples (42%). Hence in further studies 8 wt% NaN_3 supported zeolite reagents were used.

Initially the reactions were carried out in a flow reactor as reported elsewhere.[5] The styrene (1 mmol) dissolved in dry cyclohexane (20 ml) was introduced at the top of the reactor by means of an infusion pump (flow rate 20 ml h^{-1}). The liquid products were collected in a water-cooled receiver and the removal of cyclohexane did not furnish any product. The zeolite was removed from the reactor and extracted with 50 ml of methanol. Analysis of the methanol extract by GC (Hewlett Packard, 5890 Series II, gas chromatograph with a flame ionization detector, capillary column : OV-1, 25 m) showed only 29% conversion of styrene to 1-azido-1-phenylethane.

The experiments were then carried out in a magnetically stirred Teflon-lined autoclave equipped with a temperature controller. Styrene (1 mmol) dissolved in 10 ml of dry cyclohexane was added to a suspended mixture of HY-zeolite-supported NaN_3 (1 g) in cyclohexane (15 ml) and the mixture was stirred at 70 °C for 2 h under nitrogen atmosphere, after which it was filtered. The cyclohexane filtrate did not contain any dissolved matter. The product was extracted from the pores of the zeolite by washing with methanol (3 × 50 ml). Removal of methanol and further purification of the crude material by flash chromatography using an alumina column and CH_2Cl_2 as eluent furnished 84% of the corresponding azide. The recovered zeolite could be reused after NaN_3 treatment and activation.

Even in a heterogeneous reaction system where the zeolite supported NaN_3, a reactant and a solvent were mixed, the polarity of the solvent influenced the reaction rate to a significant extent. The extent of conversion of styrene and 1-phenylethanol to the corresponding azide in different solvents over HY-zeolite and HEMT supported reagents at 70 °C for 2 h was found to be in the order of cyclohexane > C_6H_6 > $CHCl_3$ > MeCN, and the results are summarized in Table 2. This could

Table 1 Comparison of the yields of various azides over different zeolite-supported NaN_3[a]

		Yield (%)[c]			
Substrate	Product[b]	HY-Zeolite	HEMT	HZSM-5	H-Zeolite beta
		84	82	76	79
		72	69	56	64
		89	73	70	80
		93	87	85	91
		76	68	71	75
		91	86	82	78
		90	92	80	76
$PhCH_2OH$	$PhCH_2N_3$	82	69	76	74
		90	94	70	86
		77	82	61	73
		86	72	65	78
Bu^tOH	Bu^tN_3	93	89	91	88
		90	81	74	79
		84	76	71	80

[a] T = 70 °C, t = 2 h. [b] All products were characterized by IR, ^1H NMR and mass spectral data. [c] Yield of isolated pure compounds.

be attributed to the stronger adsorbtion of solvent on the zeolite surface affecting (weakening) its acidic properties.

Table 2 Effect of solvent in the conversion of styrene and 1-phenylethanol to the corresponding azide over HEMT and HY-zeolite[a]

	Yield[b,c]	
Solvents	HY-Zeolite	HEMT
Cyclohexane	84 (90)	82 (94)
C_6H_6	69 (73)	76 (67)
$CHCl_3$	42 (34)	39 (30)
MeCN	9 (5)	11 (7)

[a] T = 70 °C, t = 2h. [b] Yield of isolated pure product. [c] Yield of azide from 1-phenylethanol in parentheses.

In order to compare homogeneous reagent systems with the zeolite-supported reagent system, styrene dissolved in aqueous methanol was treated with NaN_3 and unsupported HY-zeolite at 70 °C for 2 h and furnished 1-azido-1-phenylethane in low yield (14%); in the case of 1-phenylethanol the yield of the corresponding azide was only 12%. In a control experiment, triphenylmethanol (1 mmol), a molecule which cannot enter the pores of HZSM-5 due to its large size, was dissolved in 10 ml of dry cyclohexane and added to a suspention of zeolite-supported NaN_3 (1 g) in dry cyclohexane (15 ml). The reaction mixture was stirred for 2 h at 70 °C and afforded the corresponding azide in 5% yield, while over HY-zeolite (a large pore zeolite)-supported reagent the yield of the azide was 68%. This result indicates that in zeolite-supported NaN_3 reagents most of the NaN_3 is located inside the pores, not on the outside surface of the zeolites. Silica gel and alumina mediated addition of HN_3 to alkenes has been studied in the past and attempts to add HN_3 to diphenylethene in the presence of a strong acid, such as sulfuric acid, led to considerable decomposition due to the susceptability of the resulting azide to protonation and Schmidt rearrangement.[9] The observed efficient performance of HY-zeolite may be attributed to its large pore openings (0.74 nm) and three dimensional channel system and the comparitively low yields of the desired products over HZSM-5 may be due to its small pore opening (0.56 nm).[7] Zeolite-supported sodium azide, when mediating the conversion of alkenes to the corresponding azides, furnished only the Markovnikoff product.

In summary, we have established a facile heterogeneous catalytic method for the conversion of alkenes and alcohols to the corresponding azides. The positive features of these inexpensive zeolites include stability, ease of handling, lack of corrosiveness and other environmental hazards and ease of separation of the product and regeneration of the catalyst.

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