Zeolite as a reagent and as a catalyst: reduction and isomerization of alkenes by Ca Y

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Depending on the number of Brønsted acid sites present, Ca Y can act either as a reagent and reduce stilbenes to 1,2-diarylethanes or act as a catalyst and isomerize *cis*-stilbenes to the more stable *trans* form; Lewis acid sites generated by the activation process yield radical cations from stilbenes but these do not yield any stable products.

In spite of its success as an industrial catalyst, the main use of zeolite in the laboratory is still only as a drying agent.[1] Here we show that zeolite can be used to carry out some routine organic transformations. Examples presented illustrate that the characteristics of the zeolite are essentially controlled by its activation procedure.

In this study Ca Y was used.† Since the exact nature of activation determines the behaviour of Ca Y, the activation method is described in detail. In method A, a known amount of the zeolite was placed inside a preheated (*ca.* 500 °C) oven under aerated conditions and activated for *ca.* 10 h. The zeolite was taken out of the oven at that temperature, cooled for *ca.* 2–3 min in the laboratory atmosphere and dropped into a hexane solution of stilbenes **1** (10 mg) after which the resultant slurry was stirred for 1 h. Extraction of the hexane–zeolite slurry with methylene chloride gave the corresponding 1,2-diarylethanes **2** in high yield (>90%) (Scheme 1). It is important to note that the reduction is fairly facile, nearly quantitative and is devoid of side reactions.

Reduction by Ca Y of a double bond activated by method A was found to be general. For example, 1,1-diphenylethylenes, *p*-methoxystyrene, β-methyl-*p*-methoxystyrene, 1-phenylcyclopentene and 1-phenycyclohexene were reduced to the corresponding hydrocarbons by Ca Y.[2] However, when this reaction was extended to 1,4-diphenylbutadiene, a surprising rearrangement occurred. Addition of Ca Y, activated by method A, to a hexane solution of 1,4-diphenylbutadiene (10 mg), resulted in quantitative conversion to the products shown in Scheme 1. This reaction was exceptionally rapid; the reaction was complete within 5 min of addition. While we are sure that a carbocation is involved in these rearrangements, we are not certain of the details of the mechanism. Work is underway to establish the mechanism.
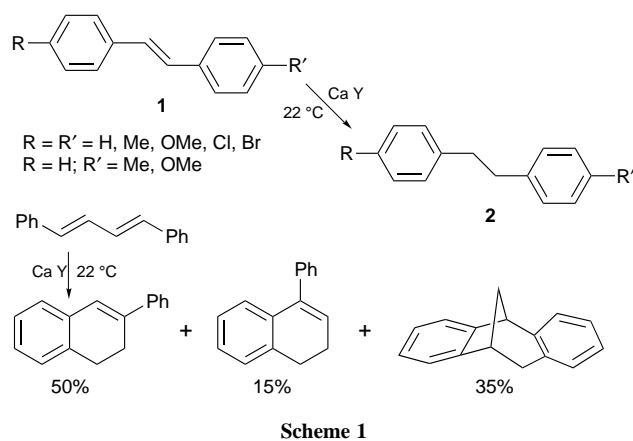
The proposed mechanism for the reduction of stilbenes is shown in Scheme 2. It is known that activation of Ca Y at 500 °C under aerated conditions generates a large number of Brønsted acid sites within the supercages of the Y zeolite.[1] Formation of H+ has been established to result from the dissociation of water by the strongly polarizing divalent cation Ca2+ (Scheme 3). By the use of a combination of Ca Y (H2O), Ca Y (D2O) and deuterated solvents (C6D12 and CD2Cl2), we showed that one of the hydrogen atoms comes from a water molecule present within the zeolite before activation and the other from the solvent. The carbocation derived from *p,p′*-dimethoxystilbene was found to be unusually stable. The diffuse reflectance spectrum of Ca Y included with *p,p′*-dimethoxystilbene showed transitions corresponding to the carbocation in the region *ca.* 300–370 nm.[3]

In the second method (method B), the zeolite was activated on a vacuum line at 450 °C. The procedure involved the following steps: a known amount of Ca Y taken in a quartz tube was degassed on a vacuum line at 5×10^{-4} Torr for about 2 h. While maintaining the vacuum, the sample was heated to 450 °C at a rate of 20 °C min^{-1} and maintained at 450 °C for *ca.* 10 h. The zeolite was cooled to room temperature and added to a hexane solution of *cis*-**1** and stirred for 3 h. Extraction of the solution gave *trans*-**1** in quantitative yield. Previous studies of alkaline earth cation exchanged zeolites have shown that the condition of activation dictates the generation of Brønsted and Lewis acid sites (Scheme 3).[1] It has been established that activation at higher temperatures (>750 °C) or at moderate temperatures (>400 °C) under vacuum results mostly in Lewis acid sites; only very few Brønsted acid sites are generated under such conditions. When we used the zeolite activated at 750 °C (method C) only isomerization was observed. Such zeolites failed to reduce the *trans*-**1**. In conclusion, the behaviour of Ca
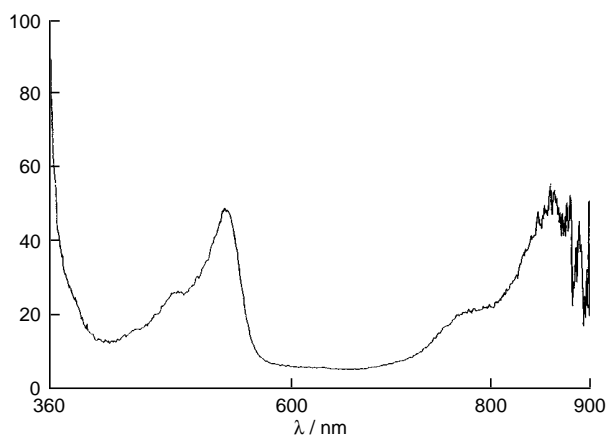
Scheme 2
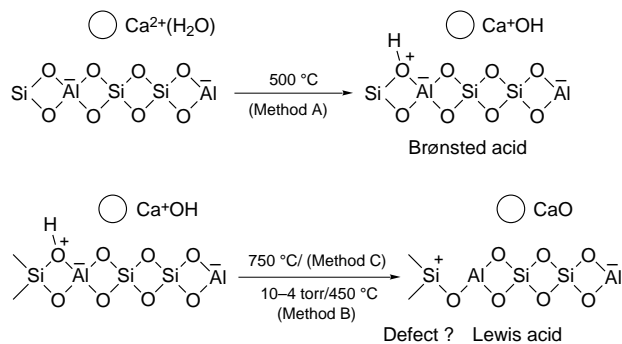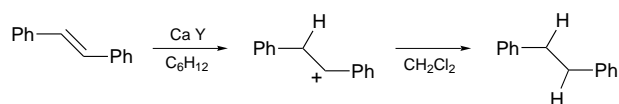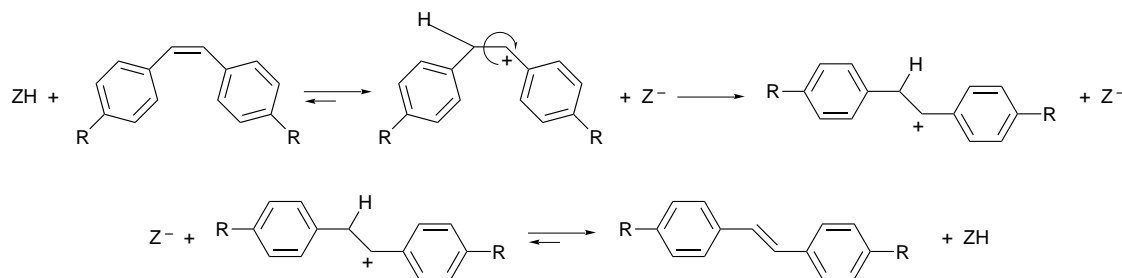
Scheme 1

Scheme 3

Scheme 4

Fig. 1 Diffuse reflectance spectrum of *p,p'*-dimethoxystilbene included within Ca Y activated at 450 °C under vacuum (10^{-4} Torr)

Y activated by method A was different from the ones activated by methods B and C.

The proposed mechanism for the geometric isomerization of **1** is shown in Scheme 4. The acid–base equilibria represented in Schemes 2 and 4, we propose, are controlled by the number of Brønsted acid sites present in Ca Y. When the number of Brønsted acid sites is disproportionately large when compared to the number of alkene molecules present in a zeolite, the acid–base equilibrium favours the permanent formation of carbocations. These carbocations have a long lifetime and abstract a hydride ion from the solvent to yield **2**. When the number of Brønsted acid sites is relatively small, not enough carbocations are generated to yield significant amounts of **2**. However, when the *cis* isomer is the guest, the protonation results in the conversion of the *cis* isomer to the thermodynamically more stable *trans* form. From the above studies it has become evident that the key to effecting selective *cis* to *trans* isomerization (without reduction) is to control the number of Brønsted acid sites within a zeolite.

In addition to the carbocation, cation radicals were also formed when stilbenes **1** were added to activated Ca Y. The extent of cation radical formation dependent on the method of activaton of Ca Y. While methods B and C gave relatively large amount of radical cations, the method A gave only minor amounts. The diffuse reflectance spectrum displayed in Fig. 1 for *p,p'*-dimethoxystilbene can clearly be identified with the radical cation of the alkene.[4] Consistent with this assignment, EPR signals were observed with the sample. The EPR spectra in all cases were broad and structureless. The radical cations generated spontaneously within Ca Y were stable for several days. Although we rule out Brønsted acid sites as possible electron acceptor sites, we have no knowledge of the nature of the electron acceptor at this time.[5]

We have shown that both carbocations and cation radicals from alkenes can be generated within Ca Y. Further, we have established that by carefully controlling the conditions of activation, one can selectively generate long-lived organic carbocations and cation radicals within such zeolites. We are in the process of identifying the electron acceptor sites within zeolites and the source of hydride ion during the reduction process.

Footnote

† Ca Y was prepared by exchanging Na Y with calcium nitrate for 12 h at 100 °C. The exchange was repeated four times, the solid filtrate was washed thoroughly with water and dried at 90 °C for *ca.* 16 h. ICP analysis indicated the exchanged zeolite to have a composition of $Si_{138.7}Al_{53.3}Na_{7.5}$-$Ca_{23.3}O_{884}$.

References

1 J. W. Ward, in *Zeolite Chemistry and Catalysis*, ed. J. A. Rabo, American Chemical Society, Washington, DC, 1976, p. 118; M. L. Poutsma, in *Zeolite Chemistry and Catalysis*, ed. J. A. Rabo, American Chemical Society, Washington DC, 1976, p. 437.
2 N. Prevost, P. H. Lakshminarasimhan, V. J. Rao and K. Pitchumani, unpublished results.
3 R. A. McClelland, C. Chan, F. Cozens, A. Modro and S. Steenken, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1337.
4 V. Ramamurthy, J. V. Caspar and D. R. Corbin, *J. Am. Chem. Soc.*, 1991, **113**, 594.
5 D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, 1964, **86**, 749; F. R. Chen and J. J. Fripiat, *J. Phys. Chem.*, 1992, **96**, 819; X. Liu, K. K. Iu, J. K. Thomas, H. He and J. Klinowski, *J. Am. Chem. Soc.*, 1994, **116**, 11 811; A. Corma, V. Fornes, H. Garcia, V. Marti and M. A. Miranda, *Chem. Mater.*, 1995, **7**, 2136.

Received, 23rd September 1996; Paper 6/06578C