Synthesis of organic sulfides using Ce-exchanged NaY catalyst

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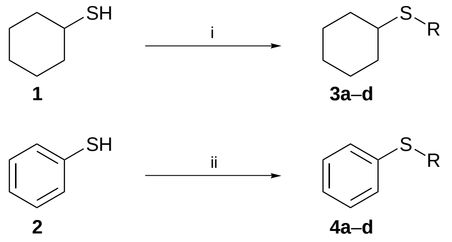
Synthesis of organic sulfides from thiols and alkyl halides is achieved using Ce-exchanged zeolite catalyst, Ce(72%)NaY.

While investigating the chemoselectivity aspects of oxidation reactions utilizing titanium silicates, we required various sulfides bearing unsaturated functionalities. There are few general methods available for the preparation of organic sulfides; however those available include phase-transfer procedures[1,2] and reactions using supported reagents on alumina.[3] Sodium sulfide impregnated on alumina facilitates the synthesis of symmetrical sulfides,[3] whereas base-catalysed alkylation of thiols using sodium hydroxide 'doped' alumina gives unsymmetrical sulfides.[3] 3-Aminopropyl(triethoxy)silane-modified basic montmorillonite clay has been used to catalyse the reaction of benzyl chloride with various thiols to produce unsymmetrical sulfides.[4] Recently, another approach has been described that uses a Pd catalyst with aryl thiocyanate-derived samarium thiolates for the synthesis of unsymmetrical sulfides.[5]

In continuation of our efforts to develop environmentally benign synthetic protocols using microwave (MW) irradiation[6] and zeolite materials,[7] we explored the synthesis of the requisite sulfides with unsaturated functionalities on solid supports. Since our attempts with sodium hydroxide 'doped' alumina and other solid supports produced only poor yields of unsaturated sulfides,[6] we focused our efforts on zeolite molecular sieves, particularly metal-exchanged Y zeolites which are weakly basic.[7a,8]

The use of various zeolite catalysts in organic transformations is a growing area of interest.[9,10] The Na form of faujasites (ex. X and Y), a class of zeolite catalyst, is almost neutral in nature. However, a basic character can be introduced by increasing the alumina content of the catalyst framework, thereby increasing the population of counter cations and their radii.[7a,11,12] Furthermore, the electrostatic interaction between the metal cation and the organic guests within the zeolite supercage has been well studied.[13,14] In this context, we have initiated a program exploiting the interactions of exchanged rare-earth cations of the faujasites with the included organic guest molecules in the supercages. Our main aim is to identify the conditions in which such an interaction could create sufficient polarization of the organic guests inside the supercages to facilitate chemical transformations. In line with our expectations, when a hexane solution of thiophenol **2** and benzyl bromide was refluxed in the presence of cerium-exchanged NaY (or NaX) zeolite, the benzyl phenyl sulfide was produced in 92% yield† (Scheme 1). These encouraging results prompted us to explore the use of the cerium-exchanged NaY zeolite, Ce(72%)NaY, for the synthesis of unsymmetrical sulfides.

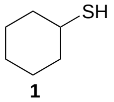
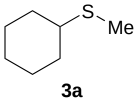
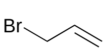
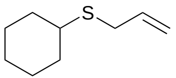
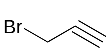
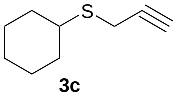
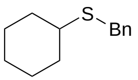
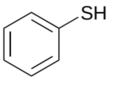
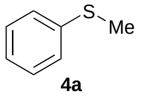
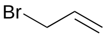
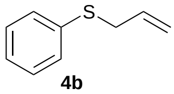
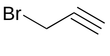
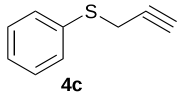
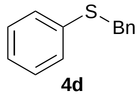


R = methyl, allyl, prop-2-ynyl and benzyl

Scheme 1 *Reagents and conditions*: i, RX, hexane, Ce(72%)NaY, reflux, 14–16 h; ii, RX, hexane, Ce(72%)NaY, reflux, 8–10 h

Briefly, the preparation of the Ce-exchanged catalyst involved the treatment of zeolite NaY[15]‡ with aqueous cerium chloride solution (prepared using double distilled and deionized water with pH adjusted to 5.0) at 95 °C for 8 h. After cooling to room temperature, the exchanged catalyst was filtered off and washed with water. The percentage of Na^+ exchange was determined (35%) by conventional gravimetric analysis of the aqueous filtrate; this procedure is repeated twice, resulting in a maximum exchange of 72%. The Ce(72%)NaY was dried at

Table 1 Synthesis of unsymmetrical sulfides using zeolite catalyst Ce(72%)NaY†

Entry	Thiols	Alkyl halides	Sulfides[a]	Yield (%)[b]
1	 **1**	MeI	 **3a**	75
2			 **3b**	83
3			 **3c**	77
4		BnBr	 **3d**	84
5	 **2**	MeI	 **4a**	82
6			 **4b**	85
7			 **4c**	79
8		BnBr	 **4d**	92

[a] Products exhibited spectral data compatible with assigned structures. [b] Isolated and unoptimised yields.

120 °C for 4 h and its crystalline structural integrity was discerned by X-ray analysis.[8a]

The freshly activated Ce(72%)NaY§ was used for the alkylation of cyclohexanethiol **1** and thiophenol **2** with a variety of alkyl halides such as iodomethane, allyl bromide, prop-2-ynyl bromide and benzyl bromide to provide corresponding sulfides in high yields (Table 1). The heterogeneous catalytic method described herein is attractive since it compares favourably with other reported protocols[2–4] in terms of yield. The reactions with thiophenol require 8–10 h to reach completion, whereas in the case of aliphatic compounds such as cyclohexanethiol, a relatively longer time period of 14–16 h is necessary.

In conclusion, we have demonstrated the versatility of cerium-exchanged NaY zeolite as an efficient catalyst for the synthesis of organic sulfides. These thermally stable crystalline inorganic materials are safe to handle and environmentally benign. Their recyclable nature and ease of manipulation, entailing a simple filtration step, illustrate some of the added advantages of zeolite catalysts.

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Footnotes

† Typical experimental procedure: Thiophenol (200 mg, 1.81 mmol), benzyl bromide (373 mg, 2.18 mmol) and freshly activated catalyst (40 mg, 20 mass% of thiophenol) in hexane (15 ml) was stirred for 12 h at reflux temperature to complete conversion. The progress of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature, the catalyst was filtered off and washed it with hexane (3 × 10 ml). The combined solution was concentrated at reduced pressure to afford benzyl phenyl sulfide in 92% (330 mg, mp 45–47 °C).

‡ Zeolites NaX and NaY were obtained from Union Carbide Corporation, USA. The SiO_2/Al_2O_3 ratio is 2.52 in NaX and 4.20 in NaY.

§ These reactions have also been carried out using Ce(72%)NaX catalyst with almost equal efficiency.

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