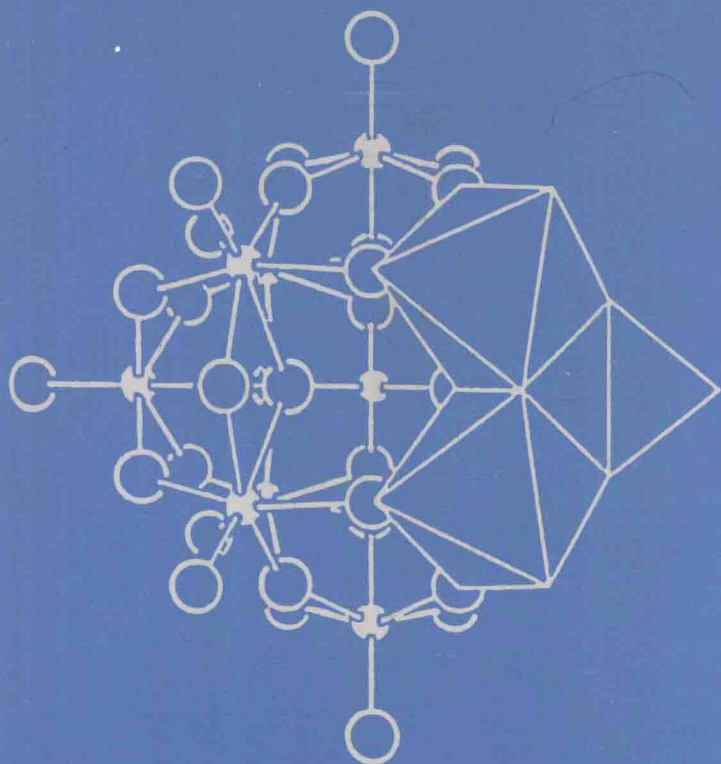


Zeolite, Clay, and Heteropoly Acid in Organic Reactions

Y. Izumi, K. Urabe and
M. Onaka



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by

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Weinheim • New York
Cambridge • Basel

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Library of Congress Card No. applied for

A CIP catalogue record for this book is available from the British Library.

Deutsche Bibliothek Cataloguing-in-Publication Data

Izumi, Yusuke : Zeolite, clay and heteropoly acid in organic reactions /
by Yusuke Izumi, Kazuo Urabe and Makoto Onaka. - Tokyo ; Kodansha :
Weinheim ; New York ; Cambridge ; Basel : VCH, 1992

ISBN 3-527-29011-7 (VCH, Weinheim . . .) ;

ISBN 1-56081-700-3 (VCH, New York) ;

ISBN 4-06-205752-2 (Kodansha)

NE : Urabe, Kazuo ; Onaka, Makoto :

This book was carefully produced. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Published jointly by
Kodansha Ltd., Tokyo (Japan),
VCH Verlagsgesellschaft mbH, Weinheim (FRG) and
VCH Publishers Inc., New York, NY (USA)

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Printed in Japan

Preface

This book is written for research chemists, process engineers and students who are interested in new catalyst materials and new catalytic methods for organic synthesis and organic processes. It describes novel catalyses and reaction-promoting functions of zeolites, clays and heteropoly acids based mainly on the recent work by the authors, stressing the remarkable catalytic performance of these catalyst materials in various types of organic reactions.

The authors, who have different research backgrounds in petrochemistry, catalyst chemistry and organic synthesis, started working together from 1980, intending to develop novel synthetic methods using zeolites, clays and heteropoly acids as reaction mediators. The reason why we selected such inorganic solids as potential catalyst materials is that they have common characteristics of well-defined molecular structure, well-arranged crystalline structure, and high cation exchange ability. These features enable us to adjust and modify their catalytic functions, such as acid and base properties, more easily and precisely than is possible with other conventional metal oxides. Such crystalline silicates and polyoxometalates often activate several types of organic reactions more effectively and more selectively than other metal oxides, more even than the conventional homogeneous catalysts, through the distinctive properties that originate in their surfaces, structural spaces, and molecular characteristics. Several approaches to catalysis described in this volume hold promise of new frontiers in synthetic and industrial organic chemistry.

Chapter 1 deals with a new approach of applying zeolites and clays to several types of liquid-phase organic synthesis as efficient catalysts and promoters, demonstrating the merits of using inorganic solids in place of homogeneous catalysts and promoters. Acid and base concerted functions of zeolite, zeolite-supported reagents, and superacid-like catalysis of metal cation-exchanged clays are described in detail.

Clay catalysts are currently the focus of a great deal of attention. In Chapter 2, new catalytic aspects of various kinds of clays will be shown through their applications to several types of organic reactions. The catalytic efficiency-determining factors of clays are described for better design of clay catalysts. Unique catalytic performance of synthetic clays and a new modification method to enhance the acidity of clay are also demonstrated.

Heteropoly acid is a unique catalyst material since it has dual catalytic functions of acid-base and oxidation-reduction. One of the authors first commercially applied heteropoly acid as a highly efficient alkene hydration catalyst for the manufacture of isopropyl alcohol. In Chapter 3, acid-base and redox molecular catalysis by heteropoly acid is described for various types of organic reactions, stressing the important role of

heteropoly anion. A novel catalytic function of heteropoly anion which enables the modification of several transition metal catalysts is also presented.

Yusuke Izumi
Kazuo Urabe
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Chapter 1 Organic Synthesis on Silicate Surfaces

1.1 Introduction

Surfaces of porous inorganic solids have been utilized as “reaction fields” mainly in vapor-phase organic reactions for producing bulk chemicals. In recent years such inorganic solids have also been used as catalysts or promoters in liquid-phase organic synthesis for fine chemicals. Several excellent reviews concerning a variety of organic reactions over inorganic solids have been published.¹⁻⁴⁾ These reviews contain many examples of better yields and higher selectivities achieved as the result of reactions proceeding on solid surfaces under reaction conditions milder than those employed in conventional homogeneous synthetic methods. It has also been widely recognized that the addition of an appropriate amount of molecular sieve zeolite to an asymmetric catalyst can provide high enantioselection.⁵⁻⁸⁾ The real function of zeolite in asymmetric synthesis, however, remains unclear. Organic chemists, therefore, have come to show much interest in incorporating the use of inorganic materials into their synthetic tactics.

At present, however, the mechanisms by which chemical and physical properties of inorganic solid surfaces influence reaction activity and selectivity have not been sufficiently elucidated so adequate candidates must often be selected by trial and error from various available solid materials. In addition, since solid surfaces show a wide spectrum of chemical and physical properties, synthetic organic chemists, who ordinarily prefer using homogeneous discrete molecules as catalysts or promoters in designing reactions, hesitate to employ heterogeneous solid materials. Nevertheless, making good use of porous solids such as silica, alumina, and zeolite as promoters in liquid-phase organic reactions provides us with certain synthetic advantages:

- 1) Easy separation of product(s) from solids by means of a simple procedure of filtration.
- 2) Adsorption or inclusion of substrate and reagent molecules into the small pores of solids with nanometer dimensions organizes the molecules in close proximity to lower the activation entropy of the reaction.
- 3) The coexisting acid and base sites on solid surfaces accelerate organic reactions synergistically; simultaneous activation of an electrophile and a nucleophile on an acid site and a base site, respectively, becomes possible.
- 4) Intrinsic pore structures of the solids discriminate between reactant molecules with respect to molecular dimensions, bringing about shape-selective organic synthesis.

Among various inorganic materials, crystalline aluminosilicates of zeolite and clay montmorillonite, which we deal with as reaction mediators in this chapter, are distinguish-

ed from others by the following characteristics: 1) well-defined crystalline structures, uniform micro cavities or interlayer spaces effecting selective reactions of organic molecules incorporated therein under steric restriction, and 2) high cation exchangeability to ensure easy adjustment of their acidic and basic properties in a wide range of pK_a values through a choice of ion-exchanged metals. By taking advantage of these features, we can systematically investigate the interrelation between solid properties and catalytic function, and we can also design tailor-made catalysts for specific reactions for practical use.

Although several reviews on the reactions using zeolites and clay minerals refer to a variety of organic reactions,⁹⁻¹⁷⁾ we will focus here on the liquid-phase organic reactions on zeolite and montmorillonite at relatively low temperatures (below 100°C) from the standpoint of synthetic organic chemists, comparing these reactions with the corresponding conventional synthetic methods under homogeneous conditions.

1.2 Organic Reactions on Zeolite

Zeolites have been investigated extensively and applied as solid catalysts almost exclusively for vapor-phase reactions at high temperatures.¹⁸⁾ In contrast, there have been few attempts to utilize zeolites as catalysts or promoters for organic synthesis in a liquid phase at moderate temperatures, partly because their acidity and basicity are often reduced by competitive adsorption of solvent molecules onto the zeolite surface.¹⁹⁾

The advantage of zeolite as a promoter is that its acid and base properties can be modified as desired through a simple procedure of ion exchange and that the organic reactions occurring inside the uniform and narrow cavities of zeolite afford higher product-, stereo- and/or regio-selectivities than reactions in homogeneous solutions.

In this section novel functions of zeolite to promote several types of liquid-phase organic reactions will be described focusing on: 1) promotion of nucleophilic substitution reactions by the cooperative function of acid and base sites on zeolite, 2) activation of inorganic reagents by dispersion on the large surface of zeolite, and 3) steric restriction of the reaction paths through small, rigid cavities of zeolite.

Among various zeolites, Y-type zeolite is generally preferable as a solid mediator for liquid-phase organic reactions because its pore window is large enough (0.74 nm) to incorporate relatively large organic molecules.

1.2.1 Reactions Promoted by Acid and Base Dual Sites of Zeolite

A. *O*-Alkylation of alcohols to ethers

O-Alkylation of alcohols with alkylating agents is not only a practical method for the synthesis of unsymmetrical ethers,²⁰⁾ but also important for protecting the hydroxyl groups of alcohols.²¹⁾ The alkylation reactions are usually conducted under strongly basic conditions via the formation of alkoxides from alcohols. However, other methods applicable under neutral conditions are awaited for the conversion of functionalized alcohols that deteriorate readily with a strong base.

Zeolite, particularly when ion-exchanged with alkali metal cations, works as a solid promoter in the benzylation of alcohols in a neutral reaction medium more efficiently than γ -alumina (Eq. (1.1)).²²⁾ This benzylation is familiar as the protection of alcoholic hydroxyl groups since the original alcohol is readily recovered by the reductive cleavage of the benzyl ether with molecular hydrogen in the presence of carbon-supported palladium catalyst.



Table 1.1 summarizes the results of the benzylation of 1-decanol in hexane solvent. Although a solid base like K_2CO_3 is ineffective for the reaction, alkali metal cation-exchanged Y-type zeolites can promote the reaction. The highest yield (73%) is obtained by K^+ -exchanged Y zeolite (hereafter abbreviated KY). In this reaction, zeolite acts not only as a promoter, but also as a base to trap the HCl produced in the course of the reaction. γ -Alumina also accelerates the reaction, but a considerable amount of the by-product dibenzyl ether is formed via hydrolysis of the reactant benzyl chloride. A homogeneous base like triethylamine is quite inactive, though much more basic than KY.

TABLE 1.1 O-Benylation of 1-Decanol with Benzyl Chloride^{a)}

Promoter ^{b)} (g)		Yield / % ^{c)}	
		Benzyl decyl ether	Dibenzyl ether
None	—	0	0
NaY	0.8	15	0
KY	0.8	73	0
CsY	0.8	62	0
$\text{Al}_2\text{O}_3^{\text{d)}$	1.2	48	7
K_2CO_3	0.5	0	0

^{a)}Reaction of 1-decanol (1 mmol) with benzyl chloride (1 mmol) in the presence of a promoter in 5 ml of hexane was performed under reflux for 5 h. ^{b)}NaY: Na^+ 100%; KY: K^+ 99%, Na^+ 1%; CsY: Cs^+ 68%, Na^+ 32%.

^{c)}Isolated yield. ^{d)} γ -Alumina for chromatographic use, pretreated at 500°C for 5 h.

Table 1.2 shows the maximum acid and base strengths of alkali metal cation-exchanged zeolites estimated by using Hammett indicators in hexane solvent.^{23,24)} It is interesting to note that zeolite KY, which is the most effective for promotion of the benzylation reaction, exhibits both moderately acidic and moderately basic strengths. This suggests that the present nucleophilic substitution reaction can be induced efficiently by the cooperative function of weakly acidic and weakly basic sites of zeolite: alcohol and benzyl chloride molecules are accessible to each other on the acid and base sites where nucleophilicity of

TABLE 1.2 Acid and Base Properties of Zeolite Y^{a)}

Acid strength $\text{p}K_{\text{a}}$	HY −8.2	CaY −8.2	>	NaY +1.5	>	KY +3.3	>	CsY +6.8
Base strength $\text{p}K_{\text{a}}$				NaY +0.8	<	KY +2.0	<	CsY +4.0

^{a)}NaY: Na^+ 100%; KY: K^+ 99%, Na^+ 1%; CsY: Cs^+ 68%, Na^+ 32%.

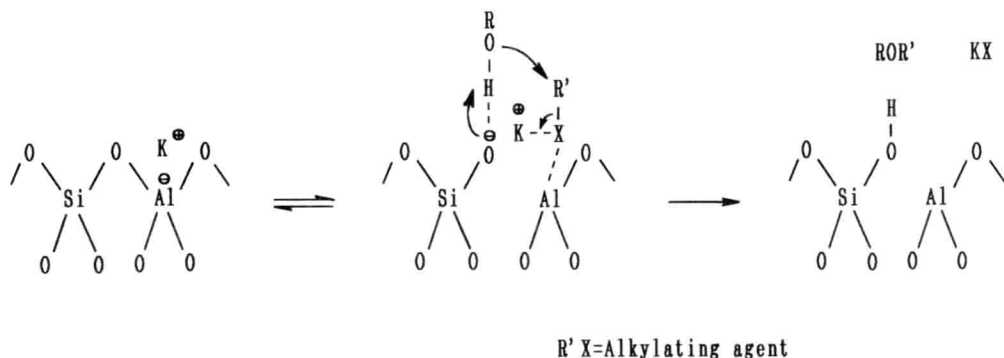


Fig. 1.1 Dual function of zeolite as acid and base.

the OH group of alcohol is enhanced by a base site, and benzyl chloride is activated by an acid site concertedly, as shown in Fig. 1.1.

The effect of solvent on the benzylation of 1-decanol with KY is demonstrated in Table 1.3. Nonpolar solvents such as hexane and carbon tetrachloride are preferable for the reaction. In benzene, diphenylmethane is formed in 28% yield based on benzyl chloride in addition to benzyl decyl ether (42% yield). The acid sites of zeolite KY are probably responsible for the formation of diphenylmethane because they catalyze a Friedel-Crafts reaction of benzene with benzyl chloride. When less nucleophilic chlorobenzene is employed instead of benzene, such an undesirable Friedel-Crafts reaction can be suppressed, and the yield of benzyl decyl ether is improved. Polar solvents like tetrahydrofuran (THF) retard the reaction drastically because THF is basic enough to poison the acid sites of KY.

TABLE 1.3 Solvent Effect on KY-promoted Benzylation of 1-Decanol^{a)}

Solvent	Benzyl decyl ether yield / % ^{b)}	1-Decanol recovery / % ^{b)}
Hexane	73	23
C ₆ H ₆ ^{c)}	42	57
C ₆ H ₅ Cl ^{d)}	77	21
CCl ₄	77	23
CHCl ₃	4	95
THF	0	100

^{a)}1-Decanol 1 mmol, benzyl chloride 1 mmol, KY 0.8 g, reflux, 5 h. ^{b)}Determined by GLC using an internal standard. ^{c)}Diphenylmethane was obtained in 28% yield as a by-product. ^{d)}The reaction was carried out at 80°C for 5 h.

Both molecular size of the alcohol and steric bulk around the hydroxyl group of the alcohol are expected to influence the rate of the benzylation reaction on zeolite. Table 1.4 summarizes the results for the benzylation of five primary alcohols with different sizes and shapes over KY under heterogeneous conditions (Method A), compared with the results obtained by a conventional method using sodium hydride and benzyl bromide in THF (Method B).

According to the CPK (Corey-Pauling-Koltun) molecular model, steric hindrance

TABLE 1.4 Effect of Alcohol Molecular Size on Benzylation

Alcohol	Method A ^{a)} yield / %	Method B ^{b)} yield / %
1-Decanol	73	73
Benzyl alcohol	57	80
Cyclohexylmethanol	58	80
Neopentyl alcohol	53	77
1-Adamantylmethanol	15	80

^{a)}Method A: alcohol 1 mmol, benzyl chloride 1 mmol, KY 0.8 g, in hexane, reflux, 5 h. ^{b)}Method B: sodium alkoxide (20 mmol) was treated with benzyl bromide (20 mmol) in THF under reflux for 5 h.

around the hydroxyl groups of the alcohols examined increases in the following order: 1-decanol < benzyl alcohol < cyclohexylmethanol < neopentyl alcohol < 1-adamantylmethanol. The results obtained by Method B show that the five alcohols have almost the same intrinsic hydroxyl group reactivity in solution. On the other hand, the reactivity of the alcohols decreases in the order of 1-decanol > benzyl alcohol \approx cyclohexylmethanol \approx neopentyl alcohol \gg 1-adamantylmethanol in the zeolite-promoted benzylation (Method A). It is assumed that narrow zeolite cavities tend to exclude bulky alcohol molecules.

The adsorption isotherms for these alcohols on zeolite KY in benzene were examined in this connection. The isotherms shown in Fig. 1.2 clearly indicate that even the most bulky 1-adamantylmethanol molecule can be adsorbed on KY as readily as the slim molecule of 1-decanol. The isotherm of 1-adamantylmethanol indicates that about 1.2 mmol of the alcohol is adsorbed on unit weight of zeolite at the alcohol concentration of 0.2 M at which the benzylation reaction is performed. Since the area occupied by a single molecule of 1-adamantylmethanol is estimated to be about 0.2 nm², 1.2 mmol of the alcohol needs a surface area of 150 m² for adsorption. The unit weight of zeolite cannot provide such a large surface area at its external surface alone. Thus 1-adamantylmethanol is mostly adsorbed not onto the external surface but inside the cavities of zeolite. The low reactivity

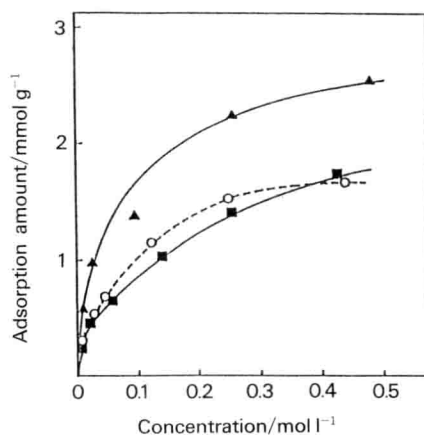


Fig. 1.2 Adsorption isotherms of alcohols on zeolite KY in benzene at 30°C. ○: 1-Decanol, ▲: cyclohexylmethanol, ■: 1-adamantylmethanol.

of 1-adamantylmethanol for the benzylation reaction in the KY system is therefore caused not by the difficulty of incorporation into the zeolite cavities, but by the steric congestion in the transition state of the reaction on the zeolite surface: 1-adamantylmethanol is so bulky that it can not readily orient itself close to a benzyl chloride molecule between the acid and base sites of KY.

KY thus provides a very effective reaction field for the selective benzylation of primary alcohols into the corresponding ethers under moderate reaction conditions. The conversion of secondary alcohols on KY is rather ineffectual since they are susceptible to dehydration into olefins as a side reaction. Besides benzyl chloride, allyl bromide and alkyl iodide are also applicable as alkylating agents (Table 1.5). 2-Methoxyethoxymethyl chloride (MEMCl) and chloromethyl methyl sulfide (MTMCl) are unsuitable because the MEM ether and MTM ether produced are further converted with 1-octanol to give dioctyl ether.

TABLE 1.5 KY-promoted Alkylation of 1-Octanol with Various Halides^{a)}

Halide	Solvent	Yield of ether / % ^{b)}
PhCH ₂ Cl	Hexane	69
CH ₂ =CHCH ₂ Br	CCl ₄	58
<i>n</i> -C ₆ H ₁₃ I	Heptane	32
CH ₃ OCH ₂ CH ₂ OCH ₂ Cl	Hexane	0
CH ₃ SCH ₂ Cl	Hexane	0

^{a)}1-Octanol 1 mmol, halide 1 mmol, reflux, 5 h. ^{b)}Isolated yield.

Experimental Procedure for Ion-exchange of Zeolite Y

A variety of cation-exchanged Y-type zeolites can be prepared using a metal chloride or metal nitrate solution. Preparation of potassium ion-exchanged Y-type zeolite (KY) from its sodium ion-exchanged counterpart (NaY) is described here as a representative example. Powdered zeolite NaY (100 g) is immersed in an aqueous 0.5 M KCl solution (1 l) at 70°C for 3 h with occasional stirring, then filtered. This procedure is repeated 10 times. The ion-exchanged zeolite is washed with deionized water until no chloride ion can be detected in the washings, dried at 110°C for 12 h, and activated at 500°C in air prior to use. The content of cations in zeolites is determined by atomic absorption analysis.

Experimental Procedure for Measurement of Acid-Base Properties of Zeolite

Acid-base properties of zeolite are measured using the following Hammett indicators (*pK_a* value): anthraquinone (−8.2), Crystal Violet (+0.8), 4-phenylazo-*N*-phenylaniline (+1.5), 4'-amino-2,3'-dimethylazobenzene (+2.0), 4-dimethylaminoazobenzene (Butter Yellow) (+3.3), 4-phenylazo-1-naphthylamine (+4.0), and Neutral Red (+6.8). Zeolite is dried at 500°C for 3 h in air. Then 0.1 g of the zeolite is placed in a test tube, and 2 ml of dry benzene is added. A few drops of a 0.1% benzene solution of the indicator are added. After one day, the color of the indicator on the zeolite is judged by the naked eye.

Experimental Procedure for O-Alkylation of Alcohol on Zeolite

Activated zeolite (0.8 g) and solvent (2 ml) under nitrogen are placed in a flask. A solution of an alcohol (1 ml) and an alkylating agent (1 mmol) in a solvent (3 ml) is added, and the suspended mixture is stirred under the conditions shown in Tables. For work-up, water (3 ml) is added, and the resulting mixture is stirred at room temperature for 0.5 h. This work-up procedure is necessary to extract completely the organic products trapped in the zeolite. The zeolite is filtered off and washed with ethyl acetate. The organic products are extracted with ethyl acetate from the filtrate. The extract is dried over sodium sulfate, filtered and analyzed.

TABLE 1.7 *N*-Alkylation of Aniline Derivatives (*p*-ZC₆H₄NH₂) with Alkylating Agents (RX) over Zeolite KY and Alumina

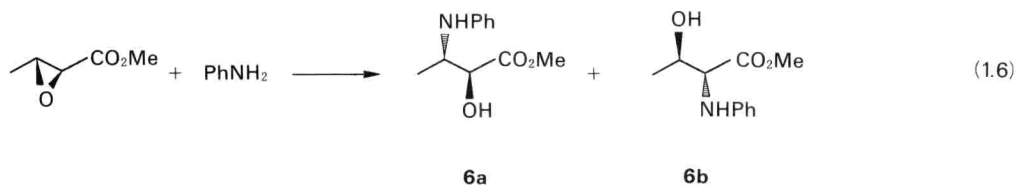
Z	Promoter	Conditions ^{a)}	Yield/ % ^{b)}	1/2
RX = Allyl bromide				
NO ₂	KY	A	79	19
	Al ₂ O ₃	A	31	66
CN	KY	A	87	25
	Al ₂ O ₃	A	40	19
CO ₂ Et	KY	A	74	7.1
	Al ₂ O ₃	A	35	13
H	KY	A	89	9.2
	Al ₂ O ₃	A	50	1.8
RX = Benzyl bromide				
NO ₂	KY	B	76	9.0
	Al ₂ O ₃	B	71	9.1
CN	KY	B	70	14
	Al ₂ O ₃	B	69	5.0
CO ₂ Et	KY	B	72	50
	Al ₂ O ₃	B	47	6.4
H	KY	C	90	14
	Al ₂ O ₃	C	60	1.4
RX = Dimethyl sulfate				
NO ₂	KY	D	55	4.6
	Al ₂ O ₃	D	38	7.3
CN	KY	D	55	3.9
	Al ₂ O ₃	D	39	4.2
CO ₂ Et	KY	D	59	6.4
	Al ₂ O ₃	D	32	2.4
Cl	KY	E	74	11
H	KY	F	58	21
	Al ₂ O ₃	F	67	1.2
Me	KY	G	68	5.9

^{a)}A: benzene, 50°C, 5 h; B: benzene, reflux, 5 h; C: benzene, 50°C, 5 h; D: toluene, reflux, 15 h; E: toluene, reflux, 12 h; F: benzene, reflux, 9 h; G: toluene, reflux, 9 h. ^{b)}Combined yield of **1** and **2**.

base, being accompanied by configurational inversion on the substituted carbon.²⁷⁾ Posner and Rogers reported that γ -alumina promoted nucleophilic ring openings of epoxides with amines, alcohols and carboxylates to give β -functionalized alcohols stereospecifically in good yields under mild reaction conditions.²⁸⁾ This efficient catalysis by alumina is assumed to be due to the cooperative function of acidic and basic sites on alumina.

To clarify the interrelation between the reaction activity of a solid catalyst and its acid and base properties, several types of ring opening of epoxides have been investigated using alkali cation-exchanged zeolites (Eqs. (1.3), (1.4), (1.5)).²⁹⁾ Table 1.8 summarizes the results for the ring openings of unsymmetrical epoxides with aniline, together with the comparative results obtained with alumina catalyst.

Amphoteric zeolites such as NaY and KY promote the ring openings as effectively as, or in some instances more efficiently than, strongly acidic HY and CaY. This means the ring openings of epoxides are accelerated by weakly acidic and weakly basic sites through

TABLE 1.9 Ring Opening of Glycidic Ester with Aniline^{a)}

Catalyst	Yield (6a + 6b) / %	6a/6b
NaY	86	42
KY	51	17
SiO ₂	69	20
Al ₂ O ₃ (basic)	53	6

^{a)}Glycidic ester 0.5 mmol, aniline 0.5 mmol, catalyst 0.6 g, in benzene, 80°C, 9 h.

Epoxide (1 mmol), amine (1 mmol), powdered activated zeolite (500°C, 1.2 g), and solvent (6 ml) are placed in a flask. The suspended mixture is heated with stirring for 9 h under nitrogen. For work-up, water is added to the flask and the resulting mixture is stirred at room temperature to recover completely the adsorbed organic products from zeolite. Then the zeolite is filtered off and washed with ethyl acetate. The organic products are extracted with ethyl acetate from the filtrate, purified by Kugelrohr (bulb-to-bulb) distillation, and analyzed.

1.2.2 Zeolite as a Reagent Support

A. Ring openings of epoxides with zeolite-supported nucleophiles

In organic synthesis, crown ethers or quaternary ammonium salts are often utilized as phase-transfer catalysts to carry water-soluble ionic reagents into the non-aqueous organic phase.³⁰⁾ An alternative method to ensure intimate contact of ionic reagents with water-insoluble organic substrates is to use so-called “supported reagents” in which ionic reagents are highly dispersed on porous solid supports such as silica gel and alumina.^{1,3,4)} Supported reagents are currently an intriguing target for research in the field of organic synthesis.

In nucleophilic substitution reactions, relatively mild nucleophiles such as alcohol and amine must ordinarily be activated with base, but reactive anionic nucleophiles as exemplified by N_3^- , Cl^- , Br^- and PhS^- can readily attack electrophiles without the aid of base. However, since these anionic nucleophiles are sparingly soluble in nonpolar organic solvents, they should be highly dispersed on supports and applied as supported reagents when the use of polar solvents is ineffectual. Concerning the supports for anionic nucleophiles, calcium ion-exchanged Y-type zeolite (CaY) is preferable because CaY not only provides a surface area ($680 \text{ m}^2 \text{ g}^{-1}$) large enough to ensure uniform dispersion of inorganic salts, but also possesses strong acid sites ($H_0 \leq -8.2$) to activate electrophiles effectively.

In this section, the usefulness of CaY-supported ionic nucleophiles in ring-opening reactions of epoxides will be discussed.

a. Zeolite-supported azide reagent

Nucleophilic substitution with azide is an important reaction for the synthesis of alkyl