

Catalysis by Metal Containing Zeolites. I: Basic Sites

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Received: March 24, 1995; June 20, 1995

Após a introdução de zeólitas como catalisadores, a preparação de zeólitas básicas e as reações por elas catalisadas são revisadas numa escala molecular, o que permite uma compreensão das reações que ocorrem dentro dos poros das zeólitas.

After introducing zeolites as catalysts, the preparation of and the reactions catalyzed by basic zeolites are reviewed on a molecular scale which permits an understanding of the reactions occurring inside the zeolite pores.

Keywords: *zeolites, basic sites, catalysis, reaction mechanism*

Introduction

The applications of zeolites in catalytic processes

In 1960 the world of catalysis gained a new perspective. Weisz and Frilette announced the "unexpected intrinsic catalytic activity" of a faujasite like synthetic zeolite¹. Although the catalytic activity of zeolitic materials was already claimed by patents in the twenties and thirties², Weisz's and Frilette's observation of a "molecular shape-selective catalysis" with large pore faujasite zeolites was the beginning of their successful application in catalytic processes. This success is demonstrated by the increase in the number of CA-referenced zeolite publications shown in Fig. 1³.

The successful application of zeolites in industrial processes is further illustrated by the consumption of 65000 tons in 1986⁴. Zeolites are mainly used in gas-oil cracking processes which have a worldwide capacity of 40 million barrels per day⁵. These processes, which include catalytic cracking, hydrocracking, paraffin isomerization and olefin isomerization, as well as catalytic dewaxing, methanol-to-gasoline (MTG) and LPG-to-aromatics (CYCLAR) conversion, were recently reviewed by Maxwell and Stark⁴.

Besides these large-scale processes where only acidic zeolites are used, a large number of potential zeolite applications, which include not only acid but also basic and redox catalysis, were developed in industrial and university laboratories all over the world. These new applications include the synthesis of intermediates and fine chemicals⁶⁻¹³.

The main subject of these papers is the macroscopic description of the catalytic processes, and less attention has been given to the reaction mechanism and the active sites of the zeolites. However, the optimization of known processes, and the conquest of new fields for the application of zeolites as heterogeneous catalysts requires the knowledge of a catalytic system at the atomic level¹⁴. Without this knowledge, zeolite catalysis appears to be something magic. Summarizing the known data on zeolite catalysis at the atomic level could transform the understanding, especially for students and researchers just entering the field of zeolite catalysis, from having a magic to a more scientific point of view.

Due to the significance of proton-exchanged zeolites as catalysts, the nature of acid sites^{15,16} and their role in catalytic processes¹⁶, as well as the reaction mechanisms of acid-catalyzed conversions¹⁷, have been the subject of various review articles¹⁵⁻¹⁷ and monographs¹⁸⁻²⁰. However, in contrast to the proton-exchanged zeolites, little literature exists about the active sites of zeolites modified with alkali metals, which can be used as basic catalysts, and zeolites modified with transition metals, which can be used as redox catalysts. Base and redox catalyses play an important role in the manufacture of intermediates and fine chemicals.

In contrast to the production of bulk chemicals in the petrochemical industry, where acidic zeolites play an important role as heterogeneous catalysts, the production of fine chemicals remains a field of homogeneous catalysis and stoichiometric methods. However, increasing environmental constraints are making prohibitive the use of classic

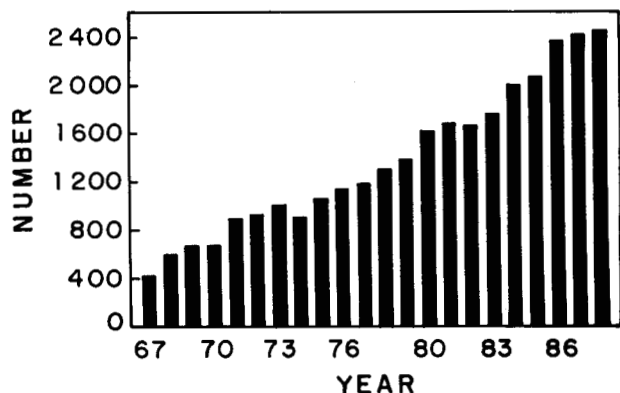


Figure 1. Number of CA-referenced zeolite publications per year³. (Reproduced with permission from Elsevier Publishers B.V., Amsterdam).

stoichiometric methods and homogeneous catalysts, which generate large amounts of contaminated effluents. The use of basic and redox active zeolites as heterogeneous catalysts can reduce these wastes and increase the economic and ecological benefits of fine chemical production.

This review will be restricted to the description of zeolites as basic catalysts, a field which might have increasing significance for the industrial production of fine chemicals. The developing field of zeolites as redox catalysts will be the subject of a later review.

The structural properties of zeolites

One advantage of zeolites is their regular intracrystalline pore system, formed by a three-dimensional network of cornersharing TO_4 -tetrahedra ($T = \text{Si}, \text{Al}$). This creates the high surface area of zeolites, with over 99% (depending on the crystallite size) inside the bulk²¹. The space of these molecular scale micropores, which depends upon the precise architecture, is responsible for the shape selective properties of the zeolitic catalysts, as outlined below. Until now more than 30 different natural and over 50 synthetic zeolite structures are known^{18-20,22,23}. However, only faujasite, ZSM-5 and mordenite have found large scale applications in catalytic processes²⁴.

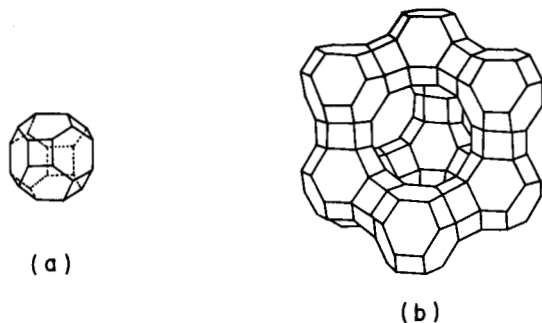


Figure 2. The faujasite structure: (a) sodalite cage; (b) super cage.

The structure of the faujasite analog synthetic zeolites X ($\text{Si}/\text{Al} = 1.5$) and Y ($\text{Si}/\text{Al} = 2.5$) was determined by Broussard and Shoemaker²⁵ and Olson²⁶. As illustrated in Fig. 2, it is formed by sodalite cages (Fig. 2a) connected via double-six rings. This leads to a three dimensional channel system with circular 12-ring apertures (diameter 7.4 Å) intersected in spherical cavities (supercages) shown in Fig. 2b, with a diameter of 11.8 Å. The 1987 consumption of zeolite Y was about $5\text{-}6 \times 10^4$ tons²⁴, corresponding to approximately 98% of the zeolites used in catalytic processes.

Shape selectivity

Shape-selective catalysis with zeolites has already been mentioned by Weisz and Frilette¹ in their first announcement on the catalytic activity of zeolites. This selectivity consists of a subtle matching of the size and shape of reactants, transition states and products with the zeolite framework. Csicsery²⁷ coined the well-known categories given below for these shape selective effects, illustrated in Fig. 3.

Reactant selectivity: only molecules which are able to enter the zeolite channel react.

Product selectivity: only molecules which are able to leave the zeolite channels are found in the product mixture.

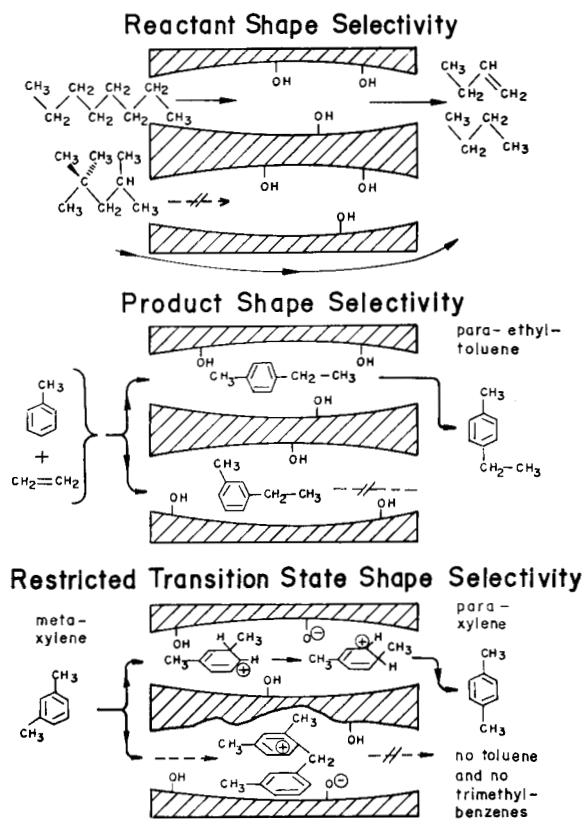


Figure 3. Examples of the three classic types of shape selectivity^{27b} (reproduced with permission from Elsevier Publishers B.V., Amsterdam).

Transition state selectivity: reactions occur only when the required transition state can be formed in the zeolite cavities.

In addition to these forms of selectivity there are some less common effects discussed in the literature¹⁷:

Concentration effect: the sorption of the substrate in the zeolite enhances its concentration by several orders of magnitude²⁸, so that bimolecular reactions are favored over monomolecular ones¹⁷.

Molecular traffic control: this kind of selectivity occurs in zeolites with different channel types, such as ZSM-5. As was outlined by Derouane and Gabelica²⁹, smaller reactant molecules will continuously diffuse inside the zeolite through the smaller sinusoidal channels, while the bulkier products desorb through the larger linear channels without hindrance from counterdiffusion effects.

Molecular circulation: Mirodatos and Barthomeuf³⁰ studied the conversion of isooctane, catalyzed by offretite with different potassium contents. They observed that a decreasing potassium content not only increased the activity, but also influenced the selectivity. They explained this occurrence by a blockage of the small cages in offretite by the potassium cations. The progressive exchange of the cations allows the isooctane molecules to enter these small cavities. This accessibility of the cavities changes the molecular flow from diffusing only along the channels to diffusing in a three-dimensional way in the crystals, giving a larger amount of smaller molecules in the cracking products.

Energy gradient selectivity: Mirodatos and Barthomeuf³¹ studied the cracking of n-heptane, n-octane and iso-octane on a variety of zeolites. They saw that the formation of light products (C_1 , C_2 , C_3) is favored for zeolites with small cavities or tortuous channels. In zeolites with large channels or cavities a larger amount of C_4 -hydrocarbons was observed. They proposed that the occurrence of secondary reactions, which determine the (C_4/C_3) and (C_4/C_2) ratios, depends on an "energetic" selectivity. The smaller and more tortuous the space in which the molecules move, the higher are the field and field gradient which favor secondary reactions. They introduced the (C_4/C_3) or (C_4/C_2) ratio as an "energy gradient selectivity" index, which is independent of factors which are related to shape selectivity.

Basic zeolites

In view of the great number of reactions which are catalyzed by acidic zeolites it is surprising that so little is known about zeolites acting as solid bases. This is much more astonishing if one considers that "shape selectivity", the great advantage of acidic zeolites, will also be present in chemical conversions catalyzed by basic zeolites. One obstacle for the preparation of such solid bases is surely the strong inherent acidity of zeolites. The presence of at least

traces of acidity which will catalyze undesired side-reactions makes it difficult to carry out base-catalyzed reactions on an industrial scale⁶ and no commercial applications have been reported up to the present⁵.

It is well known that strong Brønsted acids are conjugated to weak Brønsted bases, so that the existence of protons in zeolites has to be associated with basic sites³². From this it follows that a complete ion exchange with alkali metal ions neutralizes not only the Brønsted acid centers but also creates weak basic centers^{7,11}, so that alkali ion exchanged zeolites can be used as basic catalysts.

A further possibility for preparing basic zeolite catalysts is to use the zeolites as a support in the classic sense, by preparing nanophase alkali metal oxide within the pores of the zeolite. The preparation of nanophase cesium oxide by the decomposition of cesium acetate impregnated in dehydrated faujasite was reported by Hathaway and Davis³³. Tsuji *et al.*³⁴ demonstrated that this method also allows the preparation of other nanophase alkali metal oxides inside the zeolite cavities. These so-called "ion added" zeolites³⁴ were used as basic catalysts in a number of reactions^{12, 33-35}.

An additional method where zeolites are used as support is the impregnation of the pores with clusters of alkali atoms which can act as bases themselves. Martens *et al.*³⁶ created basic sodium clusters by thermal decomposition of sodium azide impregnated in dehydrated faujasite-type zeolite, and demonstrated their possibilities as basic catalysts^{12,36}.

Alkali Exchanged Zeolites

The determination of basicity

Early IR spectroscopic studies on alkali ion-exchanged zeolites by Bertsch and Habgood³⁷ and Ward³⁸ showed that alkali ion-exchanged and dehydrated faujasite-like zeolites possess no hydroxyl groups, with the exception of the lithium-exchanged zeolite, which shows a slight adsorption around 3700 cm^{-1} , even after evacuation for 2 h at 753 K ³⁸. After rehydration with small amounts of water a sharp band around $3715\text{--}3640\text{ cm}^{-1}$ appears, which is typical of isolated OH stretching vibrations^{37,38}. This effect is demonstrated in Fig. 4 which shows the IR spectra of NaY zeolite dehydrated at different temperatures and rehydrated with different amounts of water.

Figure 5 shows that the frequency of this OH stretching vibration decreases from 3715 cm^{-1} for Li to 3640 cm^{-1} for Cs, with the decreasing electrostatic field and potential of the cations. Bertsch and Habgood³⁷ remarked that this shift is in the same direction and on the same order as that observed by Buchanan³⁹ for the OH stretching frequencies in solid hydroxides and by Price⁴⁰ *et al.* for the spectra of water adsorbed on alkali halides. This shift to lower wavenumbers is related to an increase in the basic strength

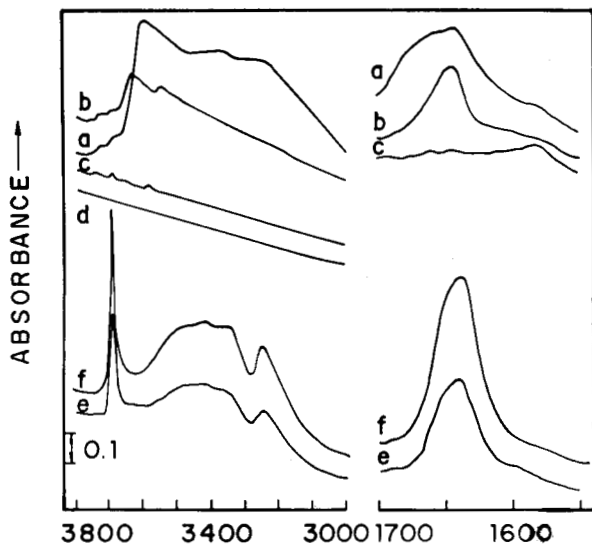


Figure 4. Spectra of the hydroxyl stretching and water bending vibrations of NaY zeolite³⁸: (a) evacuated overnight at 373 K, (b) evacuated for 2 h at 498 K, (c) evacuated for 2 h at 653 K, (d) evacuated for 2 h at 598 K, (e) 6 mol of water re-adsorbed, (f) 12 mol of water re-adsorbed (reproduced with permission from the American Chemical Society, Washington).

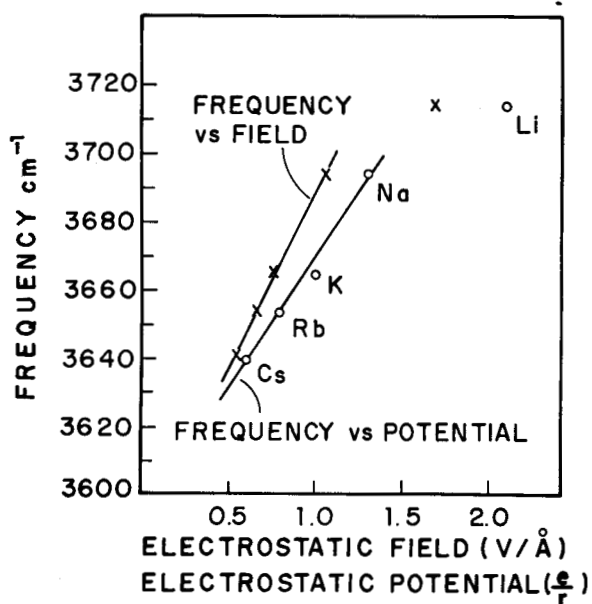


Figure 5. Frequency of the 3715-3640 cm^{-1} band vs. electrostatic field and potential as a function of the cation³⁸ (reproduced with permission from the American Chemical Society, Washington).

of the adsorption site. Bertsch and Habgood³⁷ and Ward³⁸ suggested the adsorption of water by the coordination of the lone pair electrons of the oxygen atom to the exchangeable cation, which acts as a Lewis acid, and of the hydrogen to the surface oxygen, which acts as a Brønsted base, as shown in Fig. 6.

Bertsch and Habgood³⁷ also studied the adsorption of the weak Lewis acid carbon dioxide on alkali ion-ex-

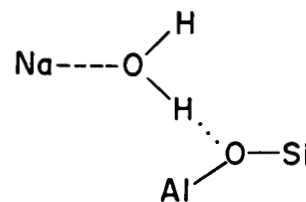


Figure 6. Adsorption of water on sodium-exchanged zeolites.

changed faujasites, and observed the formation of carbonate-like species which are formed by the coordination of the carbon dioxide molecule to a surface oxygen atom, which acts as a Lewis base.

Scokart and Rouxhet suggested the adsorption of pyrrole on basic oxides⁴¹ and zeolites⁴² as a method for the determination of the strength of their basicity. In the IR spectra, the NH stretching band is observed around 3400 cm^{-1} , which shifts to lower wavenumbers with increasing basicity. Barthomeuf⁴³ studied the basicity of several different zeolite structures exchanged with different alkali cations by this method. She was able to show that the decrease of the wavenumber of the NH stretching of pyrrole is a function of the charge of the oxygen atoms in the zeolites. Figure 7 shows this for the K-exchanged zeolites, and it has been demonstrated that aluminum-rich faujasites are the most basic catalysts.

Titration of the alkali ion-containing faujasites with pyridine in the presence of suitable indicators, a method which is outlined by Unger *et al.*⁴⁴, allowed Barthomeuf⁴³ to determine their acidic properties. Table 1 shows a proposed scale of acidity and basicity for alkali cation-exchanged faujasites, and indicates that the Na and K forms are the boundary between acidic and basic zeolites. By combining the effects of aluminum content and exchanged cations it is possible to modify the basic properties of zeolites in an almost continuous range⁴³.

Reactions catalyzed by alkali ion-exchanged zeolites

The dehydrogenation of alcohols: while acidic zeolites tend to favor the dehydration of alcohols to olefins and ethers¹², zeolites exchanged with alkali ions show a high selectivity for dehydrogenation to the corresponding aldehydes and ketones. Yashima *et al.*⁴⁵ studied the reaction of isopropanol over alkali ion-exchanged faujasites. While the Li- and Na-loaded faujasites favored dehydration, the K, Rb and Cs forms catalyzed dehydrogenation to acetone, due to their increased basicity. This dehydrogenation was suppressed by poisoning the basic sites with phenol. On the other hand, the addition of pyridine suppressed the dehydration and showed no effect on the dehydrogenation.

The mechanism for the dehydrogenation, which was suggested by Yashima *et al.*⁴⁵, is illustrated in Fig. 8. The lattice AlO_4^- interacts as a Brønsted base site with the

Table 1. Proposed scale of acid-base properties* for alkali metal-exchanged faujasites⁴³.

acid		base	
	LiY		
	NaY		
increase in acid strength	NaX	KY	increase in base strength
	KY	RbY	
		NaX	
		KX	
		RbX	
		CsX	

* Using pyridine and pyrrole to study the acidity and the basicity, respectively.

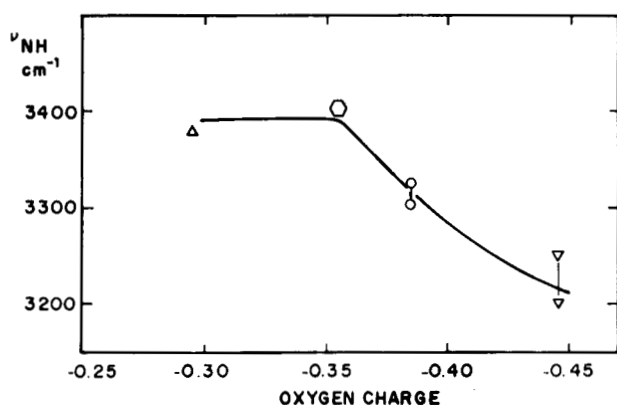


Figure 7. The change in the pyrrole NH wavenumber as a function of calculated oxygen charges for various zeolites in the K-form⁴³; (Δ) morденite, (○) L-zeolite, (○) Y-zeolite, (▽) X-zeolite (reproduced with permission from the American Chemical Society, Washington).

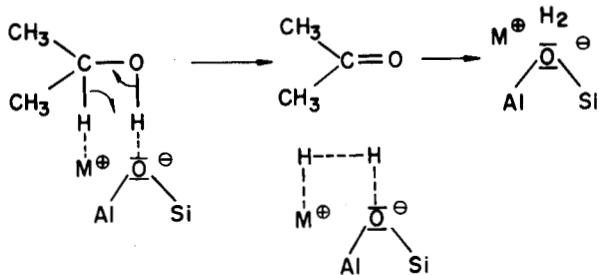


Figure 8. Dehydrogenation of methanol on alkali metal-exchanged zeolites.

hydroxyl proton of the isopropanol, while the alkali cation interacts as a weak Lewis acid with the hydrogen atom at the α -carbon. Jacobs and Uytterhoeven⁴⁶ also studied the dehydrogenation of isopropanol on Li-, Na- and K-exchanged faujasites. In contrast to Yashima *et al.*⁴⁵, they denied the action of the alkali cations as Lewis acids in this acid-base pair-catalyzed process, and suggested that iron

cations, which were present as impurities, interact as Lewis acid sites with the hydrogen at the α -carbon.

While it is generally accepted that dehydrogenation occurs at basic sites, it is doubtful that the dehydration of alcohols to olefins is catalyzed exclusively by Brønsted acid sites. Kim *et al.*⁴⁷ studied the adsorption of alcohols on TiO_2 , and showed that olefination also occurs from adsorbed alkoxide species by a β -hydrogen elimination and C-O bond cleavage. This would explain why Derewinski *et al.*⁴⁸ found propene to be the main product of the conversion of isopropanol catalyzed by alkali metal exchanged ZSM-5 zeolites. But the presence of C_4 -compounds and higher hydrocarbons in the product mixture indicated the occurrence of oligomerization and cracking processes, which are known to be catalyzed by acidic sites.

As already mentioned, the strength of the basicity increases with increasing Al content. If this is considered along with the fact that the ZSM-5 zeolites studied by Derewinski *et al.*⁴⁸ show a Si/Al-ratio of 36, the presence of basic sites in alkali ion-exchanged ZSM-5 can be excluded. This conclusion is supported by the shift of the NH-frequency of pyrrole adsorbed on Cs-exchanged ZSM-5 (Si/Al-ratio = 24), which is, as reported by Barthomeuf⁴³, the same as that observed for pyrrole on non-basic oxides. This dependency of the basicity of the Al-content limits the preparation of basic zeolites by alkali metal exchange to these which are rich in aluminum such as X- and Y-zeolites (Si/Al-ratio = 1-3).

The side chain alkylation of alkylbenzenes: another interesting reaction where the selectivity in the presence of basic zeolites is changed is the alkylation of alkylsubstituted benzenes with methanol. Acidic catalysts lead to the alkylation of the aromatic nucleus, while alkylation occurs on the side chain with basic zeolites. A number of papers deal with the alkylation of toluene⁴⁹⁻⁵⁴ and the alkylation of p-xylene⁵⁵ and aniline⁵⁶ has also been studied. It is assumed that the first step of side chain alkylation involves the dehydrogenation of methanol to the true alkylation agent, formaldehyde⁴⁹⁻⁵², which has been confirmed by infrared studies⁵⁷. As previously pointed out, this process requires the presence of an acid/base pair. Itoh *et al.*^{50,55} showed that this is also necessary for the second step: the formation of styrene by the addition of formaldehyde to the methyl group. Figure 9 illustrates the mechanism proposed by Itoh *et al.*⁵⁰, which they confirmed by quantum chemical calculations.

In the bimolecular transition state, the methyl group is adsorbed on a basic site of the zeolite and the aromatic nucleus on an acidic site, while the formaldehyde is activated by an acidic site opposite the zeolite/toluene complex (Fig. 9b). Here, the distance between the acid-base pair, which activates the toluene, and the acidic site, which activates the intermediate formaldehyde, is approximately

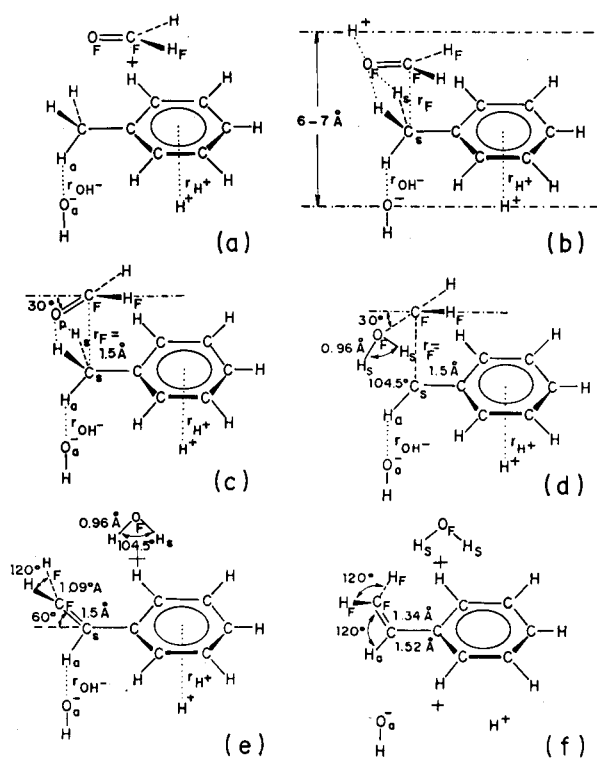


Figure 9. States during the course of the reaction of toluene and formaldehyde⁵⁰ (reproduced by permission from Academic Press Inc., Orlando).

6-7 Å, which corresponds to the channel dimensions of faujasites. The importance of this specific configuration of acidic and basic sites, which is given in the faujasite framework, explains the significantly higher activity of alkali ion-exchanged faujasites in comparison to other catalysts⁴⁹. The significance of the basic sites for the side chain alkylation is indicated by the higher selectivity towards styrene and ethylbenzene for the most basic Cs-X zeolite^{49,51-54}.

However, some authors argue that "transition state selectivity" might also be responsible for the increased selectivity^{49,54}. The large Cs cation hinders the rotation of toluene adsorbed on the Cs-faujasite, so that a transition complex involving ring attack is unlikely to occur.

The condensation between carbonyl groups and active hydrogen compounds: the condensation of n-butyraldehyde catalyzed by faujasites exchanged with different alkali and alkali earth cations was studied by Isakov and Minachev¹³. It was shown that the alkali-exchanged basic zeolites exhibited higher activity than the acidic ones. The mechanism of this reaction (aldol condensation) is given in Fig. 10.

Corma *et al.*^{58,59} studied the similar Knoevenagel condensation of benzaldehyde and derivatives of malonic esters with different pK_a -values as active hydrogen

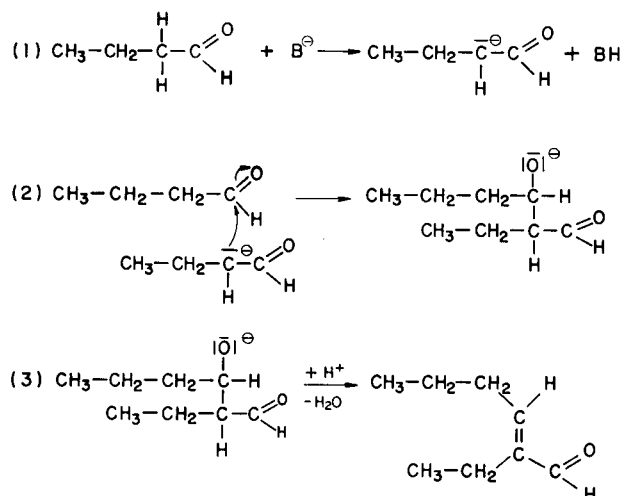


Figure 10. The mechanism of aldol condensation.

compounds. They demonstrated that for a given active hydrogen compound, the activity increased with increasing basicity of the zeolite, while the activity for a given zeolite decreased with increasing pK_a -value of the substrate used. The latter effect allowed them to determine the strength of the basic sites present in the zeolite. The number of basic sites was determined by poisoning with increasing amounts of acid.

Wierzchowski and Zatorski⁶⁰ studied the influence of pre-reaction treatments on the catalytic activity of faujasites used as catalysts for the formation of methyl methacrylate from formaldehyde and methyl propionate. Dartt and Davis¹² quoted from the above paper that the formation of strong basic sites decreased the activity, and that, for the described condensation, probably both acidic and basic sites are necessary.

The role of the acidic sites in this reaction is probably the activation and stabilization of the carbonyl compound, similar to that of formaldehyde in the assumed transition state in the side chain alkylation process of alkylbenzenes. The formation of a bimolecular transition state in the described condensation reactions is supported by the fact that Corma *et al.*⁵⁸ could describe the Knoevenagel condensation by a second order kinetic equation.

The Meerwein-Ponndorf-Verley reduction: in the Meerwein-Ponndorf-Verley reduction, aldehydes and ketones can be reduced to alcohols by means of aluminum alkoxides. It is possible to perform this reaction by using isopropanol as the reductive agent in the presence of alkali ion-exchanged zeolites as catalysts. Shabtai *et al.*^{61,62} studied this reaction with different aldehydes and observed a high selectivity in the production of the corresponding alcohols. They proposed the mechanism given in Fig. 11, which also includes the role of the cation as a Lewis acid, as discussed above.

The selectivity of this reduction is adjustable by changing the exchangeable cation. This is illustrated by the

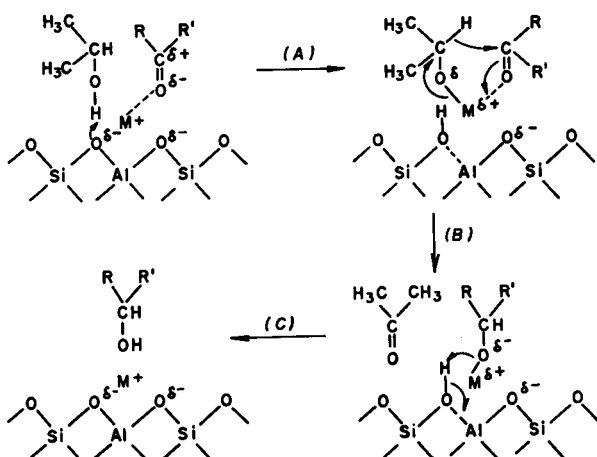


Figure 11. The proposed mechanism for the Meerwein-Ponndorf-Verley reduction with the zeolite-isopropanol system⁶² (reproduced with permission from Elsevier Publishers B.V., Amsterdam).

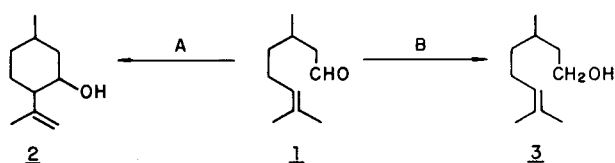


Figure 12. Reaction of citronellal catalyzed with alkali-ion exchanged X-type zeolite-isopropanol system⁶²; (A) Li-, Na-exchanged, (B) Rb-, Cs-exchanged.

following example, reported by Shabtai *et al.*^{61,62} As shown in Fig. 12, the reduction of citronellal (1) competes with an intramolecular cyclization. The use of Cs- and Rb-exchanged X-zeolites yielded 92.3% and 68.2% of the reduced citronellol (3) while Li- and Na-exchanged X-zeolites formed 87.7% and 86.0% of isopulegol (2) by an intramolecular Prins addition (Fig. 13).

Although Shabtai *et al.*⁶² argued that the steric hindrance of the larger Rb and Cs ions prevents the formation of the cyclic isopulegol, it was pointed out by Hölderich⁶ and Dartt and Davis¹² that the change in the acidic/basic properties of the zeolites used must also be considered. This interpretation seems to be correct as the Prins addition is catalyzed by acids while the reduction requires basic sites.

The conversion of methyl halides: in a recent paper Murray *et al.*⁶³ reported the conversion of methyl halides to hydrocarbons on alkali cation-exchanged faujasites.

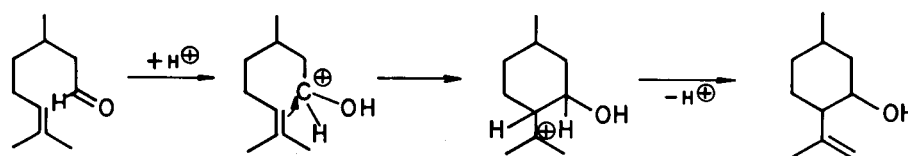


Figure 13. The formation of isopulegol from citronellal by an intramolecular Prins addition.

They monitored the interaction of the organic molecules with the zeolite framework and the alkali cation by ¹³C-NMR and ¹³³Cs-NMR spectroscopy. The ¹³C-NMR spectra demonstrated the presence of framework bound methoxy groups (Fig. 14), which are formed by displacing the leaving halogen atom through the nucleophilic attack of a Lewis base framework oxygen atom on the heteroatom-substituted carbon.

The reactivity of the methyl halides follows exactly the order which one would expect on the basis of the leaving group trend for a S_N2 reaction in solution (CH₃I > CH₃Br > CH₃Cl > CH₃OH). The catalytic activity of the alkali-exchanged faujasites increases, with the exception of the NaX zeolite, in the same order as their basicity determined by Barthomeuf⁴³ (Table 1). This demonstrates that, apart from the anomalous activity of the NaX zeolite, the reactivity of various catalyst/adsorbate combinations can be predicted by elementary chemical principles.

¹³³Cs-NMR indicated a strong interaction between the alkali metal cation and the halide, which is consistent with its role as a Lewis acid in the conversion. From their results Murray *et al.*⁶³ proposed a mechanism for the formation of ethylene from methyl halides over Cs-exchanged faujasites (Fig. 15). This mechanism includes the following four steps:

- Formation of a framework methoxy species by nucleophilic attack by a basic framework site, possible with the assistance of a Cs cation in the removal of the leaving group.
- Deprotonation of the framework methoxy group by another basic framework site.
- Activation of a second methyl halide by Lewis acid-base interaction with a Cs cation and methylation of the framework-bound alkoxy-ylide.
- Elimination of ethylene.

“Alkali Ion-Added” Zeolites

The activity of “alkali ion-added” zeolites

It was shown by Derewinski *et al.*⁴⁸ and Barthomeuf⁴³ that ZSM-5 exchanged with alkali cations does not contain basic sites. This is explained by the high Si/Al-ratio, which leads to less basic oxygen atoms with a lower negative charge, as calculated by Sanderson electronegativity^{32,43, 64}.

However, Matsumura *et al.*⁶⁵ used silicalite-I, a ZSM-5-type zeolite with a negligible Al content (Si/Al > 1500) and a quantity of Na ions approximately 40 times higher

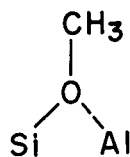


Figure 14. Framework-bound methoxy groups in an alkali ion-exchanged zeolite.

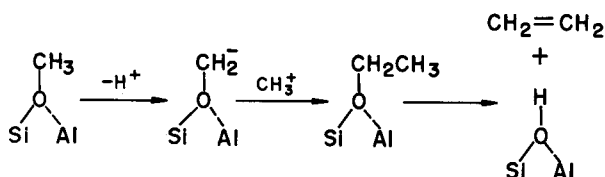


Figure 15. The proposed mechanism for the formation of ethylene from methyl iodide on Cs-exchanged X-zeolites⁶³ (reproduced with permission from the American Chemical Society, Washington).

than the Al content, as a catalyst for the dehydrogenation of methanol to formaldehyde. The neutral silicalite framework does not contain any active sites, so the catalytic activity can only originate from catalytically active sodium oxide or hydroxide particles supported in the zeolite channels and/or on the crystal surface. This is confirmed by an increased methanol conversion with increasing Na content of the catalysts and the independence from the dehydrogenation activity in the presence of trivalent cations (Al^{3+} , Ni^{3+}) in the silicalite samples studied.

Hathaway and Davis³³ generated active, basic zeolites by the decomposition of impregnated cesium acetate in the zeolite cavities. These catalysts, which exhibit an alkali cation /Al ratio greater than one, showed a higher activity for the dehydrogenation of isopropanol than ion-exchanged zeolites³³. After an intensive physico-chemical characterization of these catalysts the authors³³ proposed cesium oxide precipitated in the zeolite cavities as the active basic sites.

Tsuji *et al.*³⁴ prepared faujasites loaded with an excess of alkali metal ions using the same method as Hathaway and Davis. They studied the activity of these catalysts for the isomerization of 1-butene and found the cis/trans ratios of the products similar to those observed with alkali metal oxides as catalysts. They proposed³⁴ the presence of alkali metal oxide particles in the zeolite cavities as active centers.

Reactions catalyzed by "alkali ion-added" zeolites

The studies of Hathaway and Davis^{33,35}, Tsuji *et al.*³⁴ and Matsumura *et al.*⁶⁵ showed that "alkali ion-added" zeolites can be used as basic catalysts for the dehydrogenation of alcohols^{33,65}, olefin isomerization³⁴, alkylation of toluene with methanol³⁵, and the aldol condensation of acetone³⁵. It was shown³³⁻³⁵ that the "alkali ion-added"

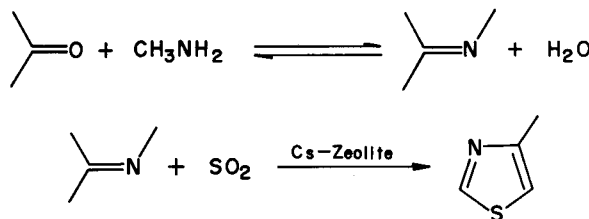


Figure 16. The formation of 4-methylthiazole over Cs-exchanged X-zeolites¹² (reproduced with permission from Elsevier Publishers B.V., Amsterdam).

zeolites (alkali ion /Al ratio > 1) possess a higher activity than ion-exchanged zeolites (alkali ion/Al ratio = 1).

A further interesting process catalyzed by "alkali ion-added" zeolites is the preparation of 4-methylthiazole over Cs ion-added zeolites, shown in Fig. 16. This process is described in a patent⁶⁶ and a conference paper⁶⁷ which is cited in Dartt and Davis's review¹². The 4-methylthiazole is an intermediate compound in the manufacture of the fungicide thiabendazole and the new process has already been successfully applied in pilot studies with ZSM-5 as the support of the basic Cs-oxide particles¹². This demonstrates the high potential of "alkali ion-added" zeolites as form selective basic catalysts, which will be especially useful in the preparation of fine chemicals and commodities.

Alkali Metal Cluster Loaded Zeolites

The preparation of alkali metal clusters in zeolites

If dehydrated and evacuated Na exchanged Y-zeolites are irradiated by γ -rays⁶⁸ or exposed to sodium vapor⁶⁹⁻⁷¹ the white aluminosilicate powder changes color to anything from light pink to black, depending on the alkali ion content in the zeolite. This is attributed to the formation of sodium clusters following the scheme given in Fig. 17.

Martens *et al.*^{36,72,73} reported that sodium clusters are also formed by the decomposition of NaN_3 impregnated in zeolites. Park *et al.*⁷⁴ recently described the preparation of ionic clusters in faujasites by stirring dry NaY zeolites under an argon atmosphere with small pieces of freshly cut alkali metal (Na or K), with or without solvents such as tetrahydrofuran, n-hexane or diethylether.

It was shown that the formation of $\text{K}^{-71,74}$ and Rb clusters^{71,75,76} is also possible. Only zeolites which contain repeating sodalite cages, such as zeolite A^{76,77}, faujasites⁶⁸⁻⁷⁴, and sodalite⁷⁸, are able to stabilize such cationic alkali metal clusters⁷⁹.

The structure of the alkali metal clusters in zeolites

Since the first reports of alkali metal clusters in zeolites^{68,69} they have been intensively studied by ESR^{69,71-75,83}, NMR^{75,82,83,85}, optical methods^{70,74,76,84}, magnetic property determination⁷⁶, and XRD techniques⁸⁶. It was shown that charged Na_5^{4+} clusters are located in the sodalite cages of the host matrix⁸⁶, as depicted in Fig. 18. At the center of

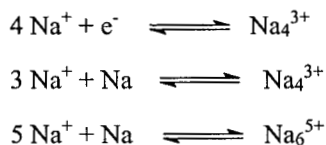


Figure 17. The formation of cationic sodium clusters.

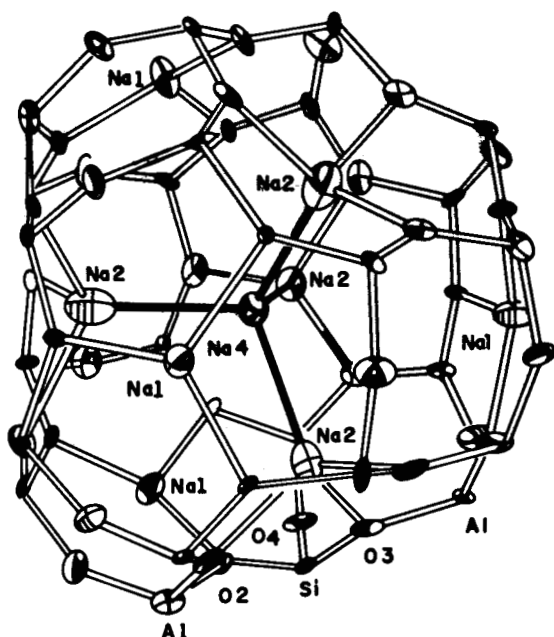


Figure 18. The structure of Na_5^{4+} clusters in a sodalite cage⁸⁶ (reproduced with permission from Elsevier Publishers B.V., Amsterdam).

some of the double six rings which connect the sodalite cages, are sodium atoms which bridge linearly between the Na_5^{4+} clusters to form agglomerations such as zig-zag chains⁸⁶.

Other authors have confirmed the presence of Na_4^{3+} clusters, which exist in sodalite cages, by ESR measurements^{71,79,83,84} (Fig. 19). These clusters can be regarded as single electron traps⁸², and could be ideal for the observation of quantum size effects.

Martens *et al.*^{36,72,73} showed through *in situ* ESR measurements that are not the charged clusters in the sodalite cages but rather the neutral sodium metal clusters located in the faujasite supercages which are responsible for the basic catalytic behavior. The amount of these catalytically active species can be optimized by the slow decomposition of NaN_3 ^{72,73}.

However, Anderson and Edwards⁸² questioned the presence of such uncharged clusters and explained the presence of the sharp ESR line, which was attributed to neutral Na clusters⁷¹⁻⁷³, as an interaction between Na_4^{3+} clusters in neighboring cages.

Although the identification of the alkali metal clusters deposited in the zeolite host might be dubious, it is obvious that zeolite frameworks are able to stabilize some unusual

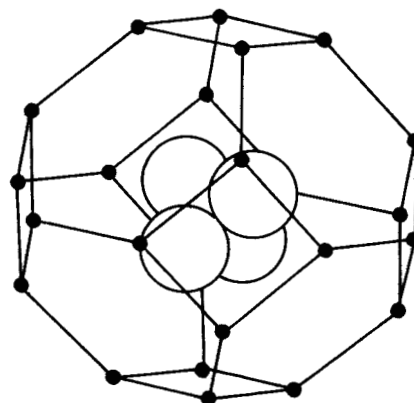


Figure 19. A sodalite cage containing a Na_4^{3+} cluster⁷¹ (reproduced with permission from the Royal Society of Chemistry, Cambridge).

clusters which may only be observed if they are hosted in the sodalite cages of zeolites⁷⁰. In a recent NMR study, Nakayama *et al.*⁸³ observed a peak which they attributed to sodide anions (Na^-) probably located in the double six rings connecting sodalite cages.

Reactions catalyzed by alkali metal cluster-loaded zeolites

It is obvious that alkali metal clusters are strong electron donors, and can act as basic sites in catalytic processes. Haag and Pines⁸⁰ studied the isomerization of 1-butene catalyzed by sodium supported on alumina. This base-catalyzed process showed none of the extensive side reactions which usually occur when acid catalysts are used for olefin isomerization⁸¹. A high selectivity towards cis-2-butene was observed, which was explained by the stabilization of the intermediate carbanion in a cyclic transition state (Fig. 20).

Martens *et al.*^{36,72,73} used this reaction to study the catalytic properties of metal cluster loaded zeolites. As is shown in Fig. 21, they obtained relative reaction rates very similar to those observed by Haag and Pines⁸⁰. In contrast to reactions catalyzed by other basic zeolites, the reaction with alkali metal cluster-loaded zeolites seems to occur via classic carbanion chemistry^{17,36}, and no acid/base pairs are involved in the olefin isomerization. The difficulties in preparing the alkali metal clusters, and their conversion to inactive oxides^{70,71} when they are exposed to air, might be an obstacle for their use as catalysts in large scale processes. However, the study of these metal clusters, which are stabilized by the zeolite matrix, is of great scientific interest^{70,82}.

Conclusions

Basic zeolites are useful catalysts for the preparation of bulk chemicals (*e.g.* side chain alkylation of alkylbenzenes, olefin isomerization), as well as for the manufacture of fine chemicals (*e.g.* preparation of 4-methylthiazole, Meerwein-Ponndorf-Verley reductions). An obstacle to their use as catalysts in large scale processes is the presence of

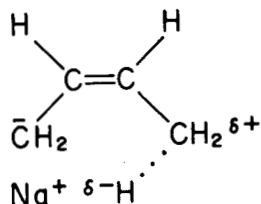


Figure 20. The stabilization of the cis-2-butene intermediate during the isomerization of 1-butene catalyzed by alkali metal clusters⁸⁰ (reproduced with permission from the American Chemical Society, Washington).

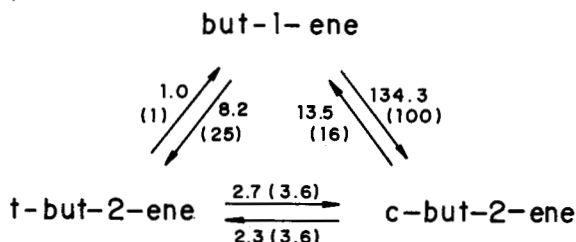


Figure 21. The relative rate constants of the butene isomerization over sodium cluster-loaded zeolites⁷³ (values for sodium clusters supported on alumina⁸⁰ in brackets) (reproduced with permission from Elsevier Publishers B.V., Amsterdam).

residual acidic sites which catalyze undesired site reactions. Thus it is doubtful that basic zeolites are an economically interesting alternative to the well-established use of acidic zeolites in large scale processes.

On the other hand, basic zeolites might be interesting catalysts for the preparation of fine chemicals. The Meerwein-Ponndorf-Verley reduction and the condensation of carbonyl groups with active hydrogen compounds show that well-known organic reactions which are employed for the conversion of functional groups in the manufacture of fine chemicals can be catalyzed by zeolites as well as by traditional homogeneous catalysts. The "heterogenization" of such processes could decrease environmental problems and increase economic benefits.

It might be helpful for the development of such new processes that Murray *et al.*⁶³ predicted the catalytic behavior of zeolitic catalysts by elementary chemical principles. This "taking the magic away" from heterogeneous catalysis will facilitate the conversion of antiquated processes to clean technologies.

Acknowledgments

Fellowships from CNPq are gratefully acknowledged. The authors thank profs. Regina Buffon and Carol H. Collins for critically reading the manuscript. The cited publishers are gratefully acknowledged for their permission to reproduce the figures in this text.

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